Studies of the Terephthalic Acid and Dihydroxy Diphenyl Sulfone Liquid Crystalline Copolymer and its Composites

by

Khurram Ahmed Khan

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

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DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

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STUDIES OF THE TEREPHTHALIC ACID AND DIHYDROXY DIPHENYL SULFONE LIQUID CRYSTALLINE COPOLYMER AND ITS COMPOSITES

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Nomenclature

LCP	Liquid crystalline polymer
PS	Polystyrene
SPS	Sulfonated polystyrene
PC	Polycarbonate
NPS	Nitrated polystyrene
DHDPS	p,p'-dihydroxydiphenyl sulfone
TC	Terephthaloyl chloride
E_c	Composite Modulus (MPa)
E_m	Modulus of pure thermoplastic matrix (MPa)
σ_c	Composite strength (MPa)
σ_m	Strength of pure thermoplastic matrix (MPa)
V_f	LCP volume fraction
w_f	LCP weight fraction
ρ_f	LCP density $\left(g/cm^3\right)$
W_f	LCP weight $\left(g\right)$
w_m	Thermoplastic weight fraction
V_m	Thermoplastic volume fraction
ρ_m	Thermoplastic density $\left(g/cm^3\right)$
W_m	Thermoplastic weight (g)

THESIS ABSTRACT

NAME OF STUDENT: KHURRAM AHMED KHAN

TITLE OF STUDY: STUDIES OF THE TEREPHTHALIC ACID AND DIHYDROXY DIPHENYL SULFONE LIQUID CRYSTALLINE COPOLYMER AND ITS COMPOSITES.

MAJOR FIELD: CHEMICAL ENGINEERING

DATE OF DEGREE: MAY 1996

A liquid crystalline polymer (LCP) was synthesized by an interfacial polycondensation reaction at room temperature from terephthaloyl chloride and p,p'-dihydroxydiphenyl sulfone. The LCP synthesized was so stable and molecularly rigid that it did not show any phase transition until it degraded at about 320°C. Composites of the LCP with polycarbonate (PC), polystyrene (PS) and sulfonated polystyrene (SPS) were formed by compression molding at a temperature at which the thermoplastic matrix was in the melt state. They were thermally analyzed by differential scanning calorimetry (DSC). Tensile specimens were cut from the compression molded plates and mechanical tests were performed. Morphology of the material systems was studied by performing scanning electron microscopy (SEM) analysis on cryogenically fractured specimens. For LCP/PS and LCP/SPS systems, a sharp two phase morphology was formed which suggested poor interfacial adhesion. Tensile strength of both systems decreased with LCP addition. The LCP/PC system also revealed a two phase morphology, however the interfaces between the LCP domains and the PC matrix were not so well defined showing better interfacial adhesion than the two previous systems studied. Stronger bonding between the LCP and PC resulted in a significant improvement in the mechanical behavior of PC by LCP addition.

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إسم الطالب :خرّم احمد خان

عنوان الرساله : دراسة بوليمر (حامض تيرفثاليك - ثنائي هيدروكسي فينيل سلفون) وخلائطه

التخصص : هندسه كيميائيه

تاريخ الشهاده : مايو ١٩٩٦م

البوليمرات التي تظهر خاصية البلوره السائله (ل . سي . ب) تمثل تقدماً علمياً مهماً ، وتدخل في تقنيات مهمه مثل الإلكترونيات والبصريات غير الخطيّه . في هذا البحث تم تصنيع أحد هذه البوليمرات وخلطه مع عدد من البوليمرات العاديه ودرست خصائص الخلائط .

تم تكوين البوليمر بتفاعل سطحي عند درجة حراره الغرفه بين تيرفثاليك كلوريد وثنائي هيدروكسي فينيل سلفون . البوليمر الناتج كان ثابتاً وجزئياته غير مرنه ، ولم يظهر أي تغير في الطور حتى درجة تحلله عند ٣٢٠ م . وتم التأكد من خاصية البلوره السائله لهذا البوليمر بملاحظه ظهر الحيود الثنائي من خلال مستقطبين متعامدين . خلط البوليمر (ل . سي . ب) مع اليو ليكاريونات ، والبوليستيرين وكبريتات البوليستيرين بطريقه المحلول ولكنها لم تنجح . ولكن طريقة التشكيل بالضغط نجحت عند درجة حراره أعلى بقليل من درجة إنصهار البوليو العادي . كبريتات البوليسترين جربت كزيادة التلاصق السطحي بين البوليمرات ، وجربت كذلك نترات البوليسترين ولكنها تحللت بفعل الحراره العاليه عند إنصهارها .

مخاليط البوليمر (ل . سي . ب) مع البوليكاربونات وكبريتات البوليستيرين والبوليستيرين حضّرت بنسبه ١ . ٥ . ١٠ . ٢٥ في المئه وتم قياس درجة التحول الزجاجيه لهذه المخاليط ، والبوليمرات النقيه ، وكذلك درجة التحلل الحراري ، وكذلك تم قياس الخواص الميكانيكيه . وإستخدام المجهر الإلكتروني لفحص التركيب الدقيق لهذه البوليمرات .

خليط بوليمر (ل . سي .ب) مع البوليستيرين لم يظهر إلتصاق سطحي جيد مما نتج عنه ضعف في الصفات الميكانيكيه لهذا الخليط . ونتج عن هذا عدم تلاحم خليط ٢٥٪ بصوره جيده .

خليط بوليمر (ل . سي . ب) مع كبريتات البوليستيرين أظهر إلتصاقاً ضعيفاً أيضاً ، ولكنه أفضل بقليل من الخليط السابق .

خليط بوليمر (ل . سي . ب) مع البوليكاربونات أظهر قوة إلتصاق جيده بين البوليكاربونات وجيبسات (ل . سي . ب) وأدى هذا إلى تحسن واضح في الخواص الميكانيكيه لهذا الخليط .

درجة ماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران – المملكه العربيه السعوديه

مايو١٩٩٦م

CHAPTER 1

INTRODUCTION

Considerable attention in the past decade has been focused on the molecular composites involving a liquid crystalline polymer (LCP) and a matrix polymer, generally a thermoplastic [Seppala et al., 1992, Dutta et al., 1990]. Exceptional strength and stiffness, low coefficient of thermal expansion, chemical resistance, excellent electrical and optical properties are some of the features of LCP [Stevens, 1991].

Liquid crystalline phase in the polymers is due to the positional and orientational order of the molecules. It is associated with molecular chains which are uniformly stiffer than in conventional polymers. This stiffness is mainly due to the presence of mesogenic units in the LCP. Mesogenic units are those repeat units which are sufficiently rigid and straight so as to polymerize to form LCP [Donald and Windle, 1992]. This rigidity is usually achieved by increasing the aromatic content of the molecules (aromatic means that the molecules contain rings of alternating single and double carbon to carbon bonds) and connecting the groups so as to optimize chain straightness.

Blends of liquid crystalline polymers with isotropic polymers can be used as an alternative for short fiber reinforced thermoplastic composites. The potential advantage of in-situ composites are that problems such as fiber-breakage, wear of the processing

equipment and rise of viscosity, occurring during the melt processing of conventional short fiber reinforced composites, can be avoided. On the contrary the melt viscosity of a thermoplastic will actually be lowered significantly upon addition of a LCP [Dutta et al., 1990].

However the drawback is that most of these molecular composites suffer poor mechanical properties due to poor dispersion at the molecular level and/or low interfacial adhesion between the LCP and the thermoplastic [Dutta et al., 1990]. The scope of this study was to design and synthesize a LCP that will exhibit strong adhesion forces with the thermoplastic.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 LIQUID CRYSTALLINITY

A liquid crystalline state is a state of matter that lies between the liquid and solid states. Materials with liquid crystalline phases consist of rod-like molecules. Liquid crystals are very common in our daily lives. They range from displays in digital watches, laptop computer screens to cell membranes in the biological systems. Synthetic liquid crystals exhibit excellent mechanical and thermal properties [Attard, 1991].

A molecule is said to be mesogenic if it is able to form a liquid crystalline phase. Polymers can form liquid crystalline phases if they contain mesogenic groups in their monomers. A liquid crystalline system is called thermotropic if it consists of mesogenic molecules alone (with no additives). The term thermotropic is particularly used to distinguish liquid crystalline phases from those, known as lyotropic, which contain solvents (addition of which reduces crystalline melting points to manageable levels) [Donald and Windle, 1992].

In thermotropic systems, the liquid crystalline phase exists only within a particular temperature range. This temperature range lies between the crystal melting point (T_m) (or in some cases where crystallinity is not observed, the glass transition temperature, T_g) and an upper transition temperature ($T_{lc \rightarrow i}$) where the liquid crystalline phase reverts to an isotropic (same properties in all direction) liquid [Donald and Windle, 1992].

To give an insight of this state of ordered liquid molecules, the thermoplastic characteristics of amorphous, crystalline and liquid crystalline polymers are shown in Fig. 1. An amorphous polymeric material contains randomly entangled chains. However a crystalline polymer contains domains in which the polymer chains are packed in an ordered array and these ordered arrays are surrounded by amorphous polymer matrix. Both amorphous and crystalline thermoplastics are rigid at low temperatures. As the temperature rises they change from glassy state to a rubbery elastomer or flexible plastic. At the molecular level this change can be defined as the ease of torsion of the backbone bonds of a molecular chain. The temperature at which this change occurs is called the glass transition temperature (T_g). At temperatures above T_g, amorphous polymers behave differently than crystalline polymers. As the temperature of the amorphous polymer is raised, the rubbery elastomeric phase gradually transforms to a soft extensible elastomeric phase, then to a gum and finally to a liquid. No sharp transitions occur from one phase to the other and only a gradual change in properties is perceptible. However for those polymers which crystallize to any extent, there is a single melting temperature, T_m.

LCPs have same type of structures below and above T_g as that of crystalline type of thermoplastics. However between a liquid crystalline temperature, T_{lc} , and T_m lies

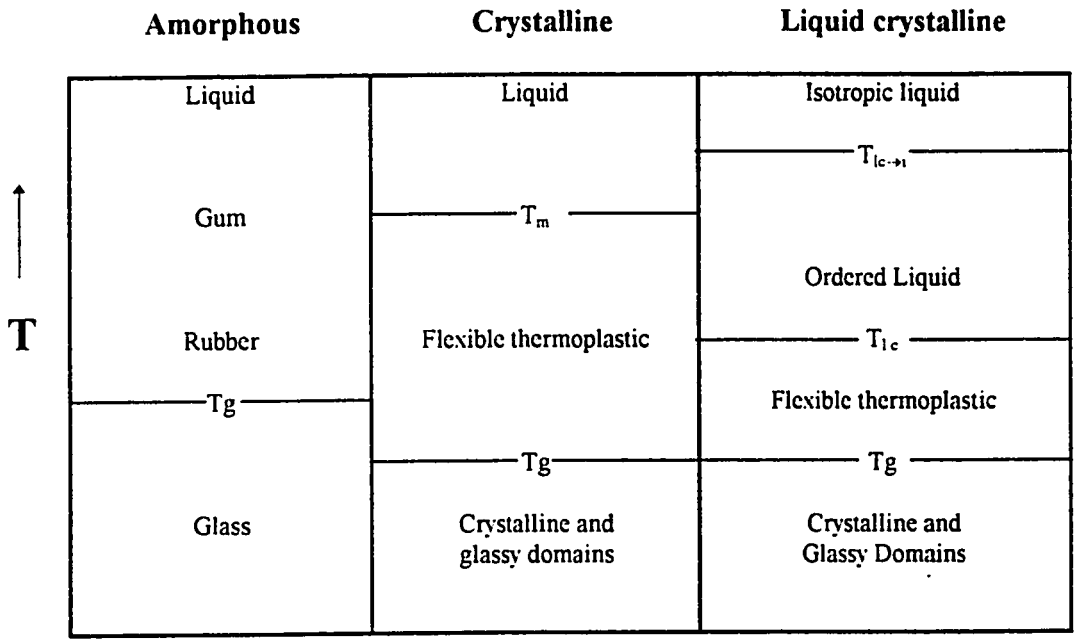


Fig. 1. Variations of different polymeric states with increasing temperature [Allcok and Lampe, 1990].

a region of ordered liquid. Above T_m the molecules lose their anistropy and behave like an ordinary isotropic liquid. However very stable and molecularly rigid LCPs might decompose before liquid crystalline to isotropic transition is observed.

2.1.1 MOLECULAR ARRANGEMENT IN LIQUID CRYSTALLINE POLYMERS

Liquid crystalline polymers are classified as nematic, cholesteric and smectic (known as Friedelian classes) depending on their molecular arrangements [Donald and Windle, 1992].

The nematic liquid crystalline polymers possess long range orientational order but only short range positional order. Such a structure is shown in Fig. 2a. The rod like molecules are aligned, not perfectly, in the direction of vector n, known as the director.

The cholesteric arrangement is illustrated in Fig. 2b [Donald and Windle, 1992]. This state is equivalent to nematic arrangement which has been twisted periodically about an axis perpendicular to the director. Chirality is associated with the presence of asymmetric carbon atoms in the liquid crystalline polymer.

Smectic phases are characterized by the possession of a layered structure on account of the segregation of the ends of the rod molecules onto common planes. There are several variants of smectic, however the two most common ones are smectic A and smectic C as shown in Fig. 2c. In smectic A (Fig. 2c(i)) the director lies along the layer normal. The molecular packing within the layers has no long range positional correlation. There is also no correlation between the lateral positions of the

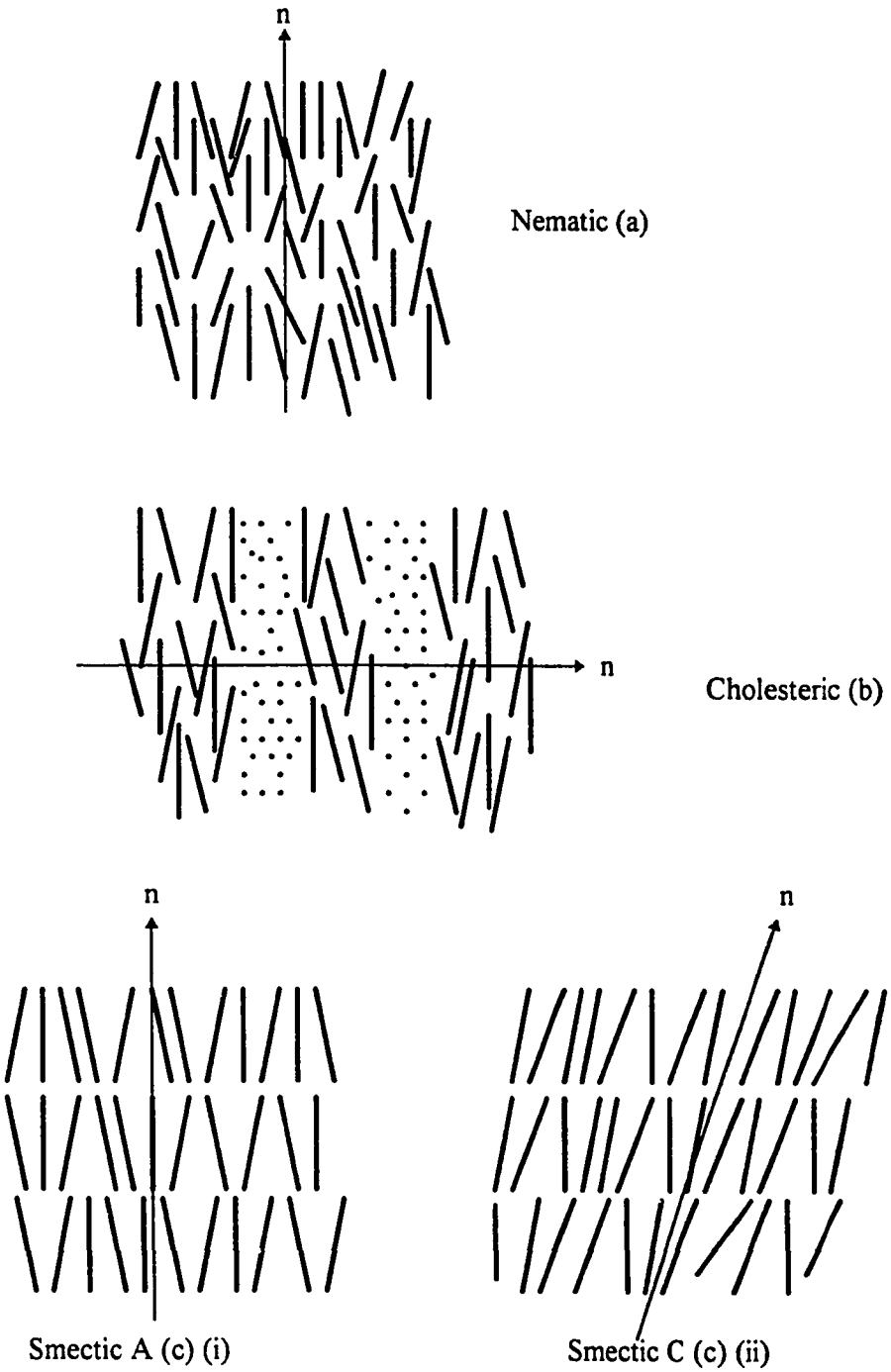


Fig. 2. Representation of the molecular arrangements in the three Friedlian classes of liquid crystals [Donald and Windle, 1992].

molecules in successive layers. Smectic C differs from smectic A in that the director is inclined at an angle to the layer normal (Fig. 2c(ii)).

2.1.2 TYPES OF LIQUID CRYSTALLINE POLYMERS

A liquid crystalline polymer can be constructed simply by linking a rigid mesogenic group in a sequence as shown in Fig. 3a. However, linking the mesogenic groups in this fashion results in high transition temperatures, T_m (or T_g) and $T_{lc\rightarrow i}$. In such a case, thermal degradation of the polymer often prevents the mesophase (liquid crystalline phase) from being observed [Donald and Windle, 1992].

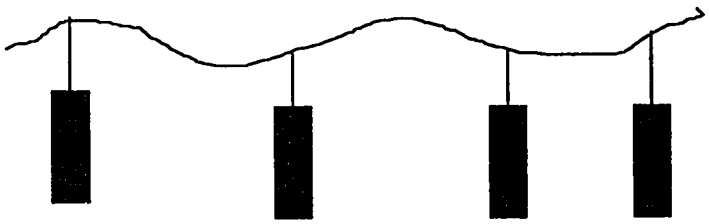
One way to reduce the transition temperatures into a useful working range without destroying the mesophase stability is to introduce more mobile linking groups between the rigid mesogenic groups or to introduce flexible spacers between the rigid groups to give a linear molecule (Fig. 3b). Another possibility is to attach the mesogenic groups as side chains to the flexible polymer chain (Fig. 3c). Transition temperatures of a LCP may also be reduced by the addition of a low molecular weight solvent [Donald and Windle, 1992]. Such LCPs are called lyotropic as mentioned earlier.

2.2 COMPOSITES OF LCP AND THERMOPLASTICS

Liquid crystalline polymers are molecularly dispersed with thermoplastics to achieve a reinforced matrix polymer that has improved properties. Another advantage of mixing a

(a) Rigid rod polymer

(b) Flexible spacers



(c) Side chain polymer

Fig. 3. Various types of Liquid Crystalline Polymer molecules [Donald and Windle, 1992].

LCP with thermoplastic is that the former acts as a processing aid. The oriented LCP domains in the composite lubricate the polymer melt and lower the melt viscosity of the blend. Therefore the processing temperatures are lower in melt blends than in thermoplastic polymers alone. This results in energy saving and less degradation of polymers that are sensitive to elevated temperatures [Dutta et al., 1990].

In order to successfully reinforce a thermoplastic polymer with a LCP, one must consider the compatibility of the LCP with the thermoplastic polymer with the aim of achieving better interfacial adhesion. Possible methods of improving interfacial adhesion are:

(i) Using side chain LCPs in which the main chain is compatible with the conventional polymer constituent in the blend and the side chain mesogenic units are compatible with the LCP constituent [Spontak and Windle, 1991].

(ii) Allowing the LCP to react with the polymer at high temperatures, as the case for the blend of polyester (LCP) with polycarbonate [Spontak and Windle, 1991].

(iii) By incorporating intermolecular hydrogen-bonding in the LCP molecule. However intermolecular H-bonding applies only to few systems. Such systems can be the ones in which the alkyl chains of the LCP contain electronegative elements such as fluorine, nitrogen and oxygen. The hydrogen atom should be sandwiched between the LCP molecule and the thermoplastic chain. These atoms (F, N, O), if present, show strong interaction with hydrogen atom causing a hydrogen bonding to occur, which improves the adhesion between the LCP and the thermoplastic [Kumar, 1992].

(iv) By attaching some strong interacting groups to the thermoplastics. Examples of this type of modification includes nitration and sulfonation of polystyrene [Makowski et al., 1975, Gauthier and Eisenberg, 1989].

2.3 REVIEW OF PREVIOUS STUDY

2.3.1 STUDY OF LCP FORMATION AND CHARACTERIZATION

The credit for the discovery of liquid crystallinity goes to Reinitzer, an Austrian botanist, who in 1888 observed peculiar melting behaviour of cholesteryl acetate and cholesteryl benzoate [Attard et al., 1991]. In the later years several other liquid crystals were synthesized and their properties were explored. For the first half of 20th century not much work was done in liquid crystals because researchers lost interest due to apparently limited applications of these substances at that time.

In 1959 Eareckson synthesized a set of copolyesters from two classes of monomers namely acid chlorides and bisphenols. Examples of acid chlorides used were terephthaloyl, isophthaloyl, sebacoyl and hydroquinone-diacetyl chlorides and the bisphenols used were bisphenol A, hydroquinone and resorcinol. He studied inherent viscosity, solubility, crystallinity and melting temperatures of these polyesters. He inferred that interfacial polycondensation technique is an excellent laboratory method for preparing high molecular weight polyphenyl esters.

In 1975, Riovello et al. synthesized a low molar mass LCP. It was p,p'- di-hydroxy-α,α'-di-methyl benzalanine. They characterized this compound as a LCP using Perkin Elmer DSC apparatus and a thermal polarizing microscope. The DSC revealed first order transitions to an anistropic liquid phase and a successive transition to an isotropic liquid. The microscopy test revealed the Schlieren texture confirming the liquid crystallinity of the compound.

In 1981 Mansour et al. synthesized some new polyarylates and copolyarylates. They utilized several monomers out of which dihydroxydiphenyl sulfone (DHDPS), bisphenol A, resorcinol and terephthaloyl chloride were the common ones used. They stated that these types of polyester films are useful in many industrial applications because of their broad range of mechanical, optical and electrical properties. They characterized the polyarylates by estimating their melting points, reduced viscosities and effect of solvents on the polyarylates.

Gupta et al., in 1982, synthesized various aliphatic-aromatic copolyesters by interfacial polycondensation and characterized them by differential scanning calorimetry, X-ray diffraction and density measurements. They observed that a decrease in T_g and melting temperature was observed on increasing the glycol content of the copolyesters.

In 1981, Antoun et al. prepared a few thermotropic liquid crystalline polymers that contained mesogenic units interconnected by flexible spacers along the main chain. They then characterized the polyesters for their liquid crystal properties. The polyesters were examinied by DSC, hot stage microscopy on a polarizing microscope, small angle light and

wide angle x-ray scattering methods and visual observation of stir-opalescence of the polymer melts.

Skovby et al., in 1990 synthesized wholly aromatic liquid crystalline main chain polyesters derived from terephthalic acid and (1-phenylethyl) hydroquinone modified with p-hydroxybenzoic acid. These polyesters were thermally investigated. It was found that these polyesters exhibit excellent thermal stability up to 400°C. They also showed that melting points could be decreased to around 200°C without any decrease in the thermal stability or the nematic range.

Some new types of polyaramides were synthesized by Kricheldorf et al. in 1992. The two monomers used were 1,4-diaminobenzene and terephthalic acid. Aromatic substituents of various lengths were also incorporated to create a new class of polyaramides. The characterization was done by conducting elemental analysis, wide-angle x-ray scattering, DSC measurements, IR and NMR spectroscopies. They found that despite relatively long substituents, meltable polyaramides were never obtained. However two homo- and two copolyamides showed a good solubility in pure N-methylpyrrolidone and compatibility with poly(vinylpyrrolidone).

2.3.2 STUDY OF BLENDS AND COMPOSITES OF LCP AND THERMOPLASTICS

The first ever blend synthesized was through the addition of a low molar mass liquid crystal to a polymer by Gebhard et al. in 1977. They were interested in the large increase

in orientational birefringence of N-p-methoxy-benzilidene-p-butylaniline (MBBA) above its nematic to isotropic phase transition temperature when it was used to swell trans-1,5-poly-pentenamer.

In 1988, Zhuang et al. studied blends of various polyethylene terephthalate/polyhydroxy benzoic acid (PET/PHB) copolyesters containing 30, 60, and 80 percent PHB with thermoplastic polymers such as polystyrene (PS), polycarbonate (PC) and polyethylene terephthalate (PET). While PS blends were found to be completely immiscible, the PC and PET blends were partially miscible. They processed the blends by compression molding, extrusion and melt-spinning. Differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and mechanical tests were conducted on the blends. It was found that blends with 10% of 60-PHB-PET exhibited significant increase in Young's modulus and tensile strength.

Kohli et al., in 1989, studied the effect of deformation history on the morphology and properties of a LCP blended with polycarbonate. The LCP was Vectra RD500, a terpolymer comprised of 52 mole percent 4-hydroxy benzoic acid (HBA), 28 mole percent 6-hydroxy-2-napthoic acid (HNA), 10 mole percent terephthalic acid and 10 mole percent hydroquinone. The addition of the LCP improved the melt processability of the thermoplastic polymer. From the DSC analysis it was observed that the T_g's of the polycarbonate and the LCP were only slightly composition dependent.

In 1991, Painter et al. formed molecular composites through hydrogen-bonding interactions. They synthesized the composites from poly(glutamates) and poly-(vinylphenol) (PVPh). The phase behaviour was studied by using FTIR and optical

microscopy. The hydrogen bond interactions was confirmed between the side-chain esters of polyglutamates and the OH group of PVPh. The results of polarizing microscope observations demonstrated that at high concentrations of rigid-rod molecules the molecules displayed anistropy.

Kim et al., in 1992, studied the mechanical properties and morphology of polymer blends of poly(ethylene terephthalte) (PET) and semiflexible thermotropic liquid crystalline polyesters (TLCP). They formed two TLCPs with long flexible spacer groups in the main chain by melt polymerization. One was a homopolymer with only decane groups (LCPHO) and the other was a copolymer with hexane or decane groups (LCPCO) between mesogenic units. These polyesters were then blended with a matrix polymer of PET. SEM revealed excellent interfacial adhesion between polyester and PET.

In 1992 Narkis et al. studied the characterization of thermotropic liquid crystalline polyester and polysulfone (PSF) blend. They studied the morphology, rheology and mechanical properties of the blends of PSF with up to 65% of a wholly aromatic LCP. The SEM revealed low interfacial adhesion in the blend. However the addition of LCP to PSF resulted in an increase in stiffness, a small increase in tensile strength and a significant improvement in processability.

Also in 1992, Son et al. studied the thermal properties of blends of liquid crystalline poly(biphenyl-4,4'-ylene sebacate) and polycarbonate (PC) by DSC. They observed that the glass transition temperature of blends decreases as the concentration of TLCP increases up to 40% by weight. The observation of a single glass transition temperature indicated that PC is miscible with TLCP in that concentration range.

Heino, et al., in 1993, processed blends of polypropylene (PP) and a liquid crystalline polymer without melting the LCP and compared them with conventional melt processed blends. At lower temperatures, where the material was processed without melting the LCP, a real composite structure was formed with solid LCP fibers in the PP matrix. When processed above the T_m of the LCP all the material was molten during processing and a composite-like blend morphology was formed inside during cooling of the oriented melt phase. The blends exhibited higher modulus than the composites, but the impact strength of the composites was significantly higher than that of the blends. Flexural tensile strength of the composites and the blends were similar.

CHAPTER 3

EXPERIMENTAL

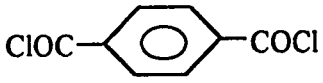
3.1 MATERIALS

The LCP was synthesized as a copolymer of terephthaloyl chloride (TC) and bis (4-hydroxy phenyl) sulfone also called dihydroxydiphenyl sulfone (DHDPS). Terephthaloyl chloride was used rather than its precursor terephthalic acid since acid chlorides are more reactive than their precursor carboxylic acids [Mansour et al., 1981].

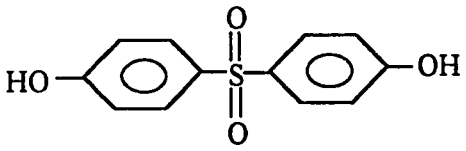
It was expected that these monomers would result in a rigid rod-like structure, imparting liquid crystallinity [Collyer, 1992]. The structural formulae of the two basic monomers are given in Fig 4. It was also expected that the oxygen atoms of the $-SO_2-$ and the $-CO_2-$ links would form hydrogen bonding with the hydrogen atoms attached to N or O present in the thermoplastic when the LCP is incorporated in a thermoplastic improving the interfacial adhesion. The details of the LCP synthesis follows.

3.1.1 PREPARATION (AND PURIFICATION) OF THE MONOMERS

Terephthaloyl chloride was formed by refluxing a mixture of 83 g of terephthalic acid in excess of thionyl chloride along with 3-4 ml of pyridine at 110°C for about 12 hrs [Eareckson, 1959]. Once the acid chloride was formed, the excess thionyl chloride was



Terephthaloyl chloride



Dihydroxy diphenyl sulfone

Fig. 4. Structural formulae of the monomers used to produce LCP.

distilled off by continuing refluxing for another hour. The terephthaloyl chloride formed was purified in several stages. The residual acid chloride was first distilled under vacuum (3 mmHg) through a short vigreux column at 115°C. Then it was mixed with dry n-hexane and distilled at 3 mmHg and 110°C. The condensed acid chloride was then dissolved in dry n-hexane at 110°C and recrystallized by letting it cool overnight. Dry n-hexane (which was prepared by distilling n-hexane with calcium hydride at 75°C) was used because moisture present in n-hexane could cause kinks in the resulting LCP. The acid chloride was lastly purified by distilling it again with dry n-hexane at 3 mmHg and 115°C. The purity of the product was tested by measuring its melting point. The temperature determined was as given in literature (81-82°C) [Turska and Jantas, 1976].

The other monomer, bis(4-hydroxy)phenyl sulfone, was 96% pure as supplied. 350 g of this monomer was mixed with 200 ml of acetone and 50 ml of dry n-hexane and ethyl ether each. The solution was heated until all the monomer was dissolved and then allowed to cool. This process of recrystallization purified the monomer further upto 98%.

3.1.2 SYNTHESIS OF LCP

LCP was initially synthesized by three different routes as listed below.

(i) LCP synthesis with toluene as the solvent [Eareckson, 1959]: An equimolar ratio of the monomers, dihydroxy diphenyl sulfone (DHDPS) and terephthaloyl chloride (TC), were used. 0.05 moles of DHDPS was weighed out and dissolved in 100 ml of 0.1M NaOH. It was then diluted with 300 ml of water. The solution was charged in a blender. Then 3 g of sodium dodecyl sulfate in 30 ml of water was added to the blender while it

was stirred slowly. It acted as a dispersing agent in the reaction. On the other hand 0.05 moles of TC was dissolved in 150 ml toluene and the solution was also charged in the blender. The reaction mixture was then blended at high speed for 5 minutes. The reaction was carried out at room temperature. The reaction mixture was then poured into excess of acetone so as to coagulate the product. After leaving the system overnight, the slurry was filtered off and washed with excess of water to remove occluded salts and detergent. This was followed by repeatedly washing with methanol and acetone to remove unreacted monomers and toluene. This method gave higher conversion of LCP as compared to the other two methods given below. Therefore this method was chosen for further synthesis of LCP in this study.

(ii) LCP synthesis with triethylamine as the medium [Vinogradova et al., 1971]: 0.01 moles of each of the two monomer were seperately dissolved in 25 ml of tetrahydrofuran (THF). The solution of DHDPS+THF was charged in a beaker. The temperature was maintained at 40°C and the solution was stirred continuously with a magnetic stirrer. First 2.50 g of triethylamine and then TC+THF solution was also added to the beaker The resulting reaction mixture was stirred for 1 hour at 40° C. Excess of water was added to quench the reaction. The resulting solution was then filtered, vacuumed and dried.

(iii) LCP synthesis with pyridine as the medium [Eareckson, 1959]: Again equimolar quantities of TC and DHDPS (0.01 moles each) were dissolved seperately in 25 ml of THF. To the solution of DHDPS in THF, 1.98 g of pyridine was added. The resulting solution was stirred with a magnetic stirrer maintaining the temperature at 40°C. This was

followed by the addition of TC/THF solution. The final reaction mixture was stirred for one hour at 40°C. Water was then added to quench the reaction. The product was filtered and vacuumed until it was dried.

3.1.3 PREPARATION OF THE THERMOPLASTICS

The thermoplastics used in this study are polycarbonate (PC) supplied by the BDH Company, polystyrene (PS) supplied by SABIC and modified polystyrene by nitration and sulfonation.

3.1.3.1 Preparation of PC

Polycarbonate was received in the form of plasticized beads. These PC beads were converted in powder form so as to have intimate mixing with the LCP while making the composites. To do so 120 g of PC beads were dissolved in excess of dimethyl formamide (DMF). Dissolving the PC beads in DMF also led to the removal of the plasticizer additive in PC. It was then heated at 50°C while stirring continued until all the PC was dissolved. This viscous solution was added slowly to excess of methanol. PC was precipitated out in thin strings and left overnight to soak in methanol. Methanol was drained and the PC was then dried in vacuum at 80°C for 4 hours. Finally it was crushed and powdered in a milling machine (Technilab Instruments Micro-Mill).

3.1.3.2 Preparation of PS

General purpose polystyrene beads were also converted to PS powder for blending

with LCP during film fabrication process. For that purpose 120 g of polystyrene beads were dissolved in excess of methylene chloride. The system was maintained at 40°C while stirring continued until all the polystyrene was dissolved. The viscous solution was then added slowly to excess of methanol. The PS that precipitated out in thin strings was left overnight to soak in methanol. Methanol was then drained and the PS was then dried in vacuum at 80°C for 4 hours.

3.1.3.3 Nitration of Polystyrene

Polystyrene was modified according to the procedure given by Gauthier and Eisenberg, 1989, by attachment of the $-NO_2$ group at the para position of the benzene ring in the repeat unit of polystryene. Addition of polarizing group ($-NO_2$) was expected to induce compatibility in the composites of polystyrene and LCP, as also suggested by Gauthier and Eisenberg.

General purpose polystyrene (GPPS) was first dissolved in 2064 ml of 3:1 volume ratio of nitrobenzene and 1,2-dichloroethane. The mixture of 1:1 volume ratio of nitric acid and sulfuric acid was stirred at 20°C by means of a water bath and then added slowly to the GPPS solution over a period of 15 minutes. The temperature of the resulting solution was maintained at 20±2°C for 24 hours with continuous stirring. Then the reaction was quenched by adding excess of distilled water. The two (aqueous and organic) layers formed were separated in a seperating funnel. The aqueous layer was discarded. Excess of methanol was added to the organic phase containing nitrated polystyrene (NPS).

The solution was left for 48 hours to remove nitrobenzene from NPS. NPS was seperated, washed with methanol, and then dissolved in excess of dimethyl formamide (DMF) to remove any trapped nitrobenzene. The solution was added slowly to excess of methanol to precipitate the NPS out, while stirring continued. This NPS was then dried in vacuum at 80°C for 7 hours. It was then powdered in the micro-milling machine.

3.1.3.4 Sulfonation of Polystyrene

GPPS was sulfonated according to the procedure of Makowski et al., 1975, by attaching -SO_3H group at the para position of the benzene ring in the repeat unit of polystyrene. The sulfonating group was attached because it was expected to improve the interfacial adhesion by forming hydrogen bonding with the LCP chain in the composites of polystyrene and LCP. It has been reported that about 8% sulfonation is achieved through that procedure [Makowski et al., 1975]. A low level of sulfonation is preferrable since sulfonation of polystyrene at high levels causes a substantial rise in viscosity resulting in difficulties in processing even at high temperatures.

The sulfonating agent used was acetyl sulfate which was prepared by adding 198 ml of 1,2-dichloroethane to 38 ml of acetic anhydride. The mixture was cooled to 10°C and to it 14 ml of concentrated sulfuric acid was added. On the other hand 104 grams of polystyrene was dissolved in 490 ml of 1,2-dichloroethane and heated to 50°C. It was then mixed with 35 ml of acetyl sulfate prepared earlier. The resulting solution was stirred for 60 minutes at 50°C. Reaction was terminated by the addition of 25 ml of methanol. The

sulfonated polystyrene (SPS) was isolated by steam stripping. This steam stripping technique was somewhat different than the conventional method used.in a way that pure nitrogen gas was purged through the solution containing SPS while the whole system was maintained at 70°C. The nitrogen was purged in order to enhance the removal of organic solvents from SPS. The polymer mass was pulverized with water in a blender, filtered, washed and dried in vacuum at 90°C. It was then powdered in the milling machine.

3.2 COMPOSITE FABRICATION

The possibility of solution blending the LCP and the thermoplastics (PC, PS, NPS, SPS) was checked first. Various solvents such as chloroform, acetone, dimethyl formamide (DMF), tetrahydrofuran (THF), phenol, acetic acid, concentrated sulfuric acid, dimethyl sulfoxide (DMS) and 1,2-dichloroethane were tried. None of these trials was satisfactory. Composites of LCP with the thermoplastics were then fabricated by compression molding at a temperature above the melting point but below the degradation temperature of the thermoplastics. Sheets at about 0.7 mm in thickness were casted from PC, PS, NPS, SPS, and composites of 1%, 5%, 10% and 25% LCP with these thermoplastics. The details of the procedure follows.

The LCP and the thermoplastic powders were first mixed roughly (in proportion) in a micromilling machine for about 5 minutes. On the other hand, two stainless steel plates were wrapped seperately with aluminium foil. This was done to avoid the sheets from sticking onto the steel plates during compression molding. A square metallic mold (11.5

cm × 11.5 cm) was placed on one of the steel plates covered with aluminium foil. The composite powder was then evenly spread in the mold and the system was placed in the compression molding machine (Wabash, Model 75-2424-4TM). A schematic of the compression molding system is given in Fig. 5. Enough time was given for the thermoplastic to melt. Then the second steel plate was placed on the mold and the whole system was compressed at a specified temperature for a fixed time. The system was then cooled to a lower temperature which was maintained for a specified duration. After that the system was cooled to room temperature and the force released. The operating parameters used for different composite systems are given in Table 1.

Table 1. Operating conditions specified for the film fabrication process.

System	Operating	Operating	Annealing	Annealing
PC and PC/LCP	225/245	6	165	30
PS and PS/LCP	225/270	6	165	30
SPS and PS/LCP	215	6	165	30
NPS and NPS/LCP	225	6	165	30

3.3 MATERIALS CHARACTERIZATION

3.3.1 CROSSED POLARIZED MICROSCOPY

Unlike a normal liquid, which would appear black when viewed through a crossed polarized microscope, the mesophase appears to be brightly colored [Templer, 1991].

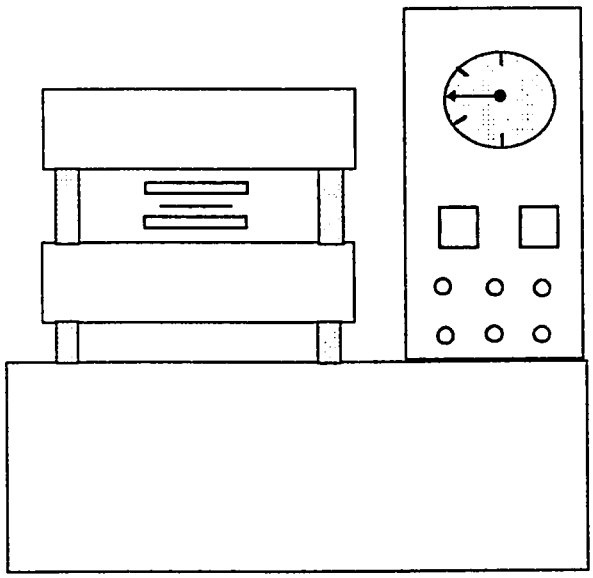


Fig. 5. The compression molding machine used in this study to produce the composites.

Crystals have a definite structure a repeating three dimensional pattern of atoms or molecules so one might expect some of them to be birefringent. Liquids, on the other hand, have no particular arrangement of their atoms or molecules, which are free to move about randomly. Therefore liquids have just one refractive index and normally appears black through crossed polarizers [Templer, 1991].

The LCP to be examined for liquid crystallinity was dissolved in concentrated sulfuric acid and then precipitated by adding a small amount of distilled water to it. A small sample from the white precipitate was placed between the crossed polarizers (Fig. 6) and observed through a light microscope with a 100X magnification.

3.3.2 MELTING POINT TEST

The melting and/or degradation temperatures of the LCP and the thermoplastics used in this study were measured by utilizing a melting point apparatus (Electrothermal Melting Point Apparatus). It was necessary to have an estimate of these temperatures in order to determine the operating temperature range for compression molding.

3.3.3 DENSITY ESTIMATION

The densities of pure PC, PS and SPS were estimated from their compression molded sheets. Pure LCP density was estimated from the difference between the densities of 25%

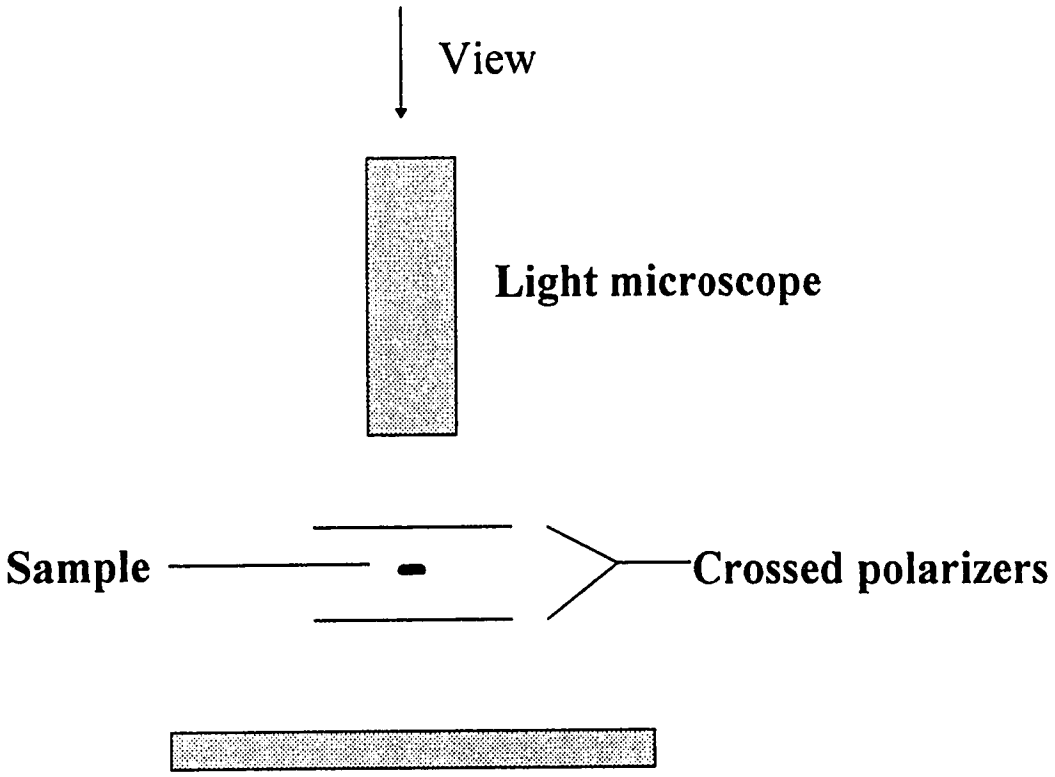


Fig. 6. LCP sample viewed through crossed polarizers with a magnification of 100×.

LCP/PC and 25% LCP/SPS sheets and the densities of pure thermoplastics determined earlier. An arithmetic average of the two values was taken as the LCP density.

Small rectangular pieces were cut from the compression molded sheets using a sharp knife edge. These pieces were weighed individually in a (Mettler 2000) weighing balance. The volume of each rectangular piece was estimated by measuring its length, width and thickness using a high precision digital caliper. Taking the ratio of mass to volume gave the value of density.

These experimentally determined density values were found to be in close agreement with the literature values. The results are shown in Table 2. The details of calculations for density estimation are given in Appendix A.

Table 2. The densities of the polymers used in this study.

	ρ(calculated) g/cm^3	ρ(Crawford, 1987) g/cm^3
PS	1.04	1.05
SPS	1.05	-
PC	1.105	1.15
LCP	1.48	-

3.3.4 MECHANICAL CHARACTERIZATION

Compression molded sheets were first cut into equal size rectangular strips. These rectangular strips were milled into ASTM tensile specimen standard D 638M-89 (Type M II) [Annual Book of ASTM Standards, 1992] by a milling machine (IPT Test Specimen Milling Machine, Model 1285). The configuration of the tensile specimen is given in

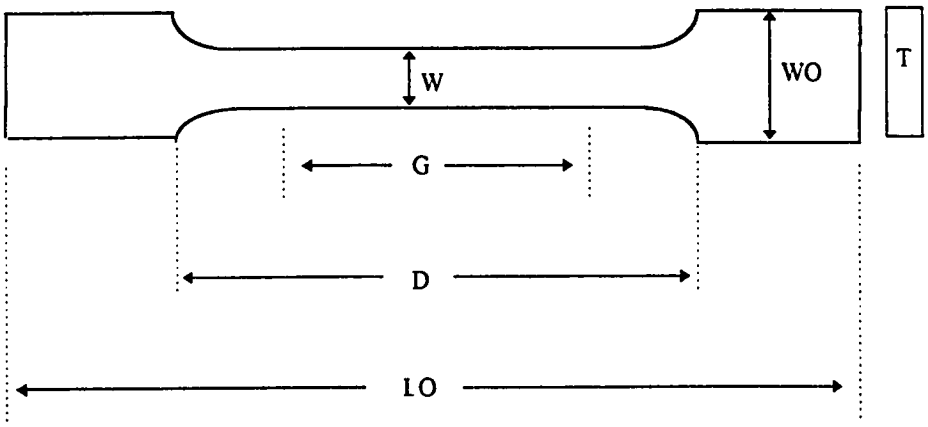
Fig. 7. The tensile tests were conducted on an Instron 1196 mechanical testing system at a displacement rate of 0.1 mm/min.

3.3.5 DIFFERENTIAL SCANNING CALORIMETRY

Thermal analysis of the materials were done by utilizing a Differential Scanning Calorimeter (Perkin Elmer DSC-4). Samples weighing in the range of 5-7 mg were encapsulated in a small aluminium pan and heated under an inert atmosphere of argon. The heating rate was 20°C/min and the temperature range covered was from 50 to 320°C. Thermograms for pure LCP, thermoplastics and their composites were obtained through a Perkin Elmer Plotter.

3.3.6 SCANNING ELECTRON MICROSCOPY

To investigate the interfacial adhesion between the LCP and the thermoplastics and the shape of the LCP particles in the matrix, fractured surfaces at cryogenic temperature (in liquid nitrogen) and tensile fractured surfaces were observed by scanning electron microscopy (SEM). The experimental system used for SEM analysis was JSM-840 Scanning Misroscope located at the Research Institute of King Fahd University of Petroleum and Minerals.



W	Width of Narrow Section	6.5 mm
WO	Width of Overall	27 mm
LO	Length Overall	115 mm
D	Distance Between Grips	65 mm
G	Gage Length	45 mm
T	Thickness	0.7-0.9 mm

Fig. 7. Tensile test specimen cut from the compression molded sheets of the composites.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 STRUCTURES OF LCP, NPS, AND SPS

As the experimental details were given earlier, the liquid crystalline polymer was formed from its two monomers, terephthaloyl chloride and dihydroxy diphenyl sulfone in a 1:1 mole ratio. The structural formula of a repeat unit of LCP is given in Fig. 8. This structure confirmed liquid crystallinity by exhibiting birefringence through crossed polarizers (Fig. 9).

Nitrated polystyrene was formed using pure polystyrene, nitrobenzene and equivolume ratio of concentrated nitric acid and concentrated sulfuric acid, as the procedure details were given in Experimental section. Fig. 10 shows structural formula of a repeat unit of NPS.

Sulfonated polystyrene was formed from acetyl sulfate (sulfonating agent) and concentrated sulfuric acid. Again refer to Experimental section for details. Structural formula of a repeat unit of SPS is given in Fig. 11.

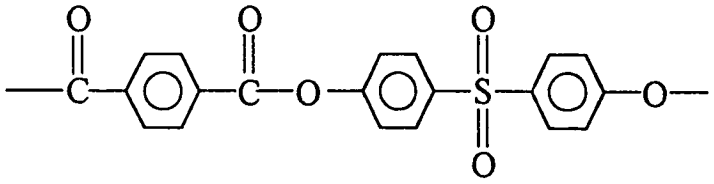


Fig. 8. Structural formula of a repeat unit of LCP

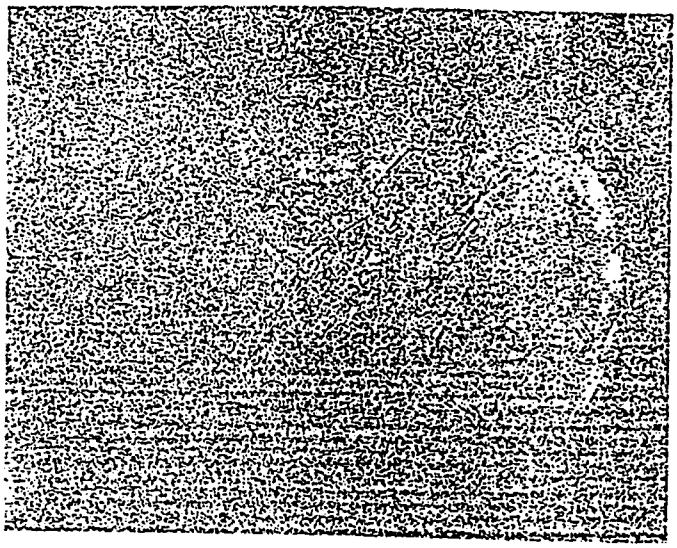


Fig. 9. Birefringence observed in pure LCP placed between crossed polarizers at a magnification of 100×.

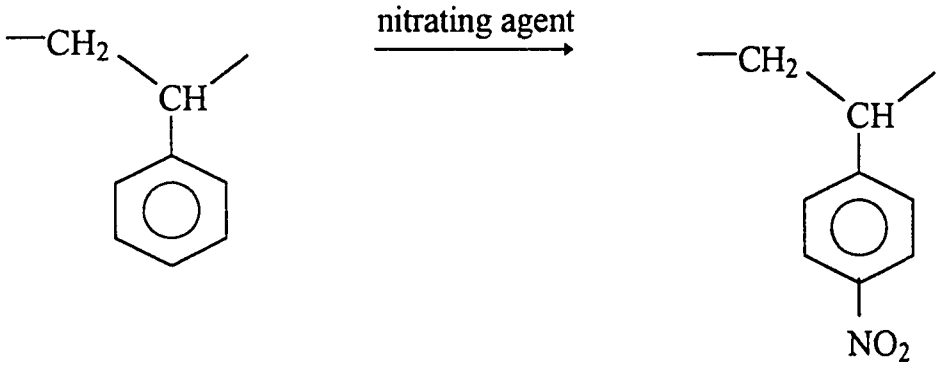


Fig. 10. Structural formula of a repeat unit of nitrated polystyrene (NPS).

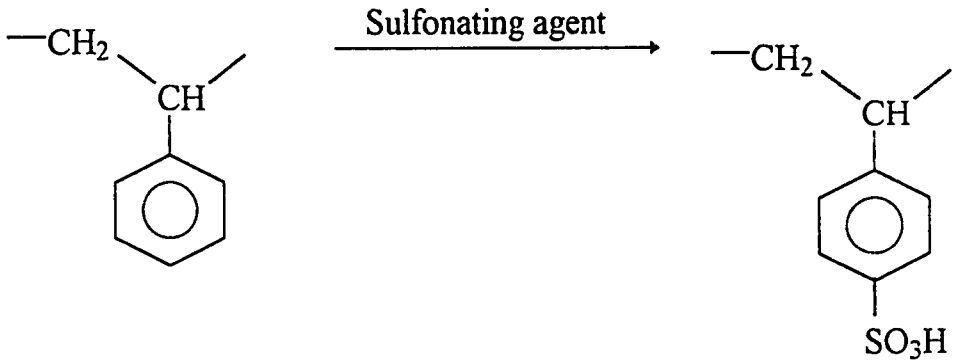


Fig. 11. Structural formula of a repeat unit of sulfonated polystyrene.

Elemental analysis was performed on LCP, NPS and SPS by Carlo Erba Elemental Analyzer in Research Institute at KFUPM. Calculated (from the structures given above) and experimentally determined weight percents of elements present in LCP and NPS were not significantly different as listed in Table 3. However, for the case of SPS about 11% sulfonation was achieved. This was higher than the level of sulfonation (7%) reported by Makowski et al., 1975, probably due to the lower temperature used in our study for the removal of organic solvents (purging nitrogen gas through the SPS solution at 70°C rather than using the conventional steam stripping at 100°C). Higher temperature might result in the breakage of SPS product back into its reactants.

Table 3. Experimental and calculated values of percents of elements present in LCP, NPS and SPS.

	% C		% H		% N		% S	
	EXP	CALC	EXP	CALC	EXP	CALC	EXP	CALC
LCP	60.8	63.1	3.4	3.2	-	-	8.8	8.5
NPS	63.7	64.4	4.7	4.69	9.4	9.39	-	-
SPS	55.37	52.17	4.52	4.34	-	-	1.9	17.4*

* Based on 100% sulfonation

4.2 MELTING AND DEGRADATION POINT TESTS

Melting and/or degradation points for LCP, SPS, NPS, PC and PS were determined using Electrothermal Melting Point Apparatus. These two temperatures were important in

determining the processing temperature range for plate fabrication. Table 4 lists the melting and degradation temperatures for the polymers used in this study. In the case of NPS, degradation and melting occurs simultaneously. Therefore composite fabrication was not possible for LCP/NPS system. In the case of LCP, melting temperature was not observed. The LCP started to degrade at around 320°C. For that reason, pure LCP plate was not possible to fabricate.

Table 4. Melting and degradation temperatures of the polymers used.

	PC	PS	SPS	NPS	LCP
Melting temperature °C	220	220	210	280	-
Degradation temperature °C	285	280	240	300	320

4.3 THERMAL ANALYSIS

Fig. 12 shows the plots of endothermic input (dQ/dt) versus temperature for the LCP/PC system. T_g's for pure PC, 1% LCP/PC, 5% LCP/PC, 10% LCP/PC and 25% LCP/PC were slightly different ranging from 145 to 150°C. It is not clear whether this slight change in T_g is due to instrumental error or some miscibility between the two phases. Also no T_g was detected for pure LCP. Likewise Fig. 13 shows the thermograms of LCP/PS system. No shift in T_g was observed as the weight percent of LCP was increased. The T_g value for pure PS and LCP/PS system was around 100°C.

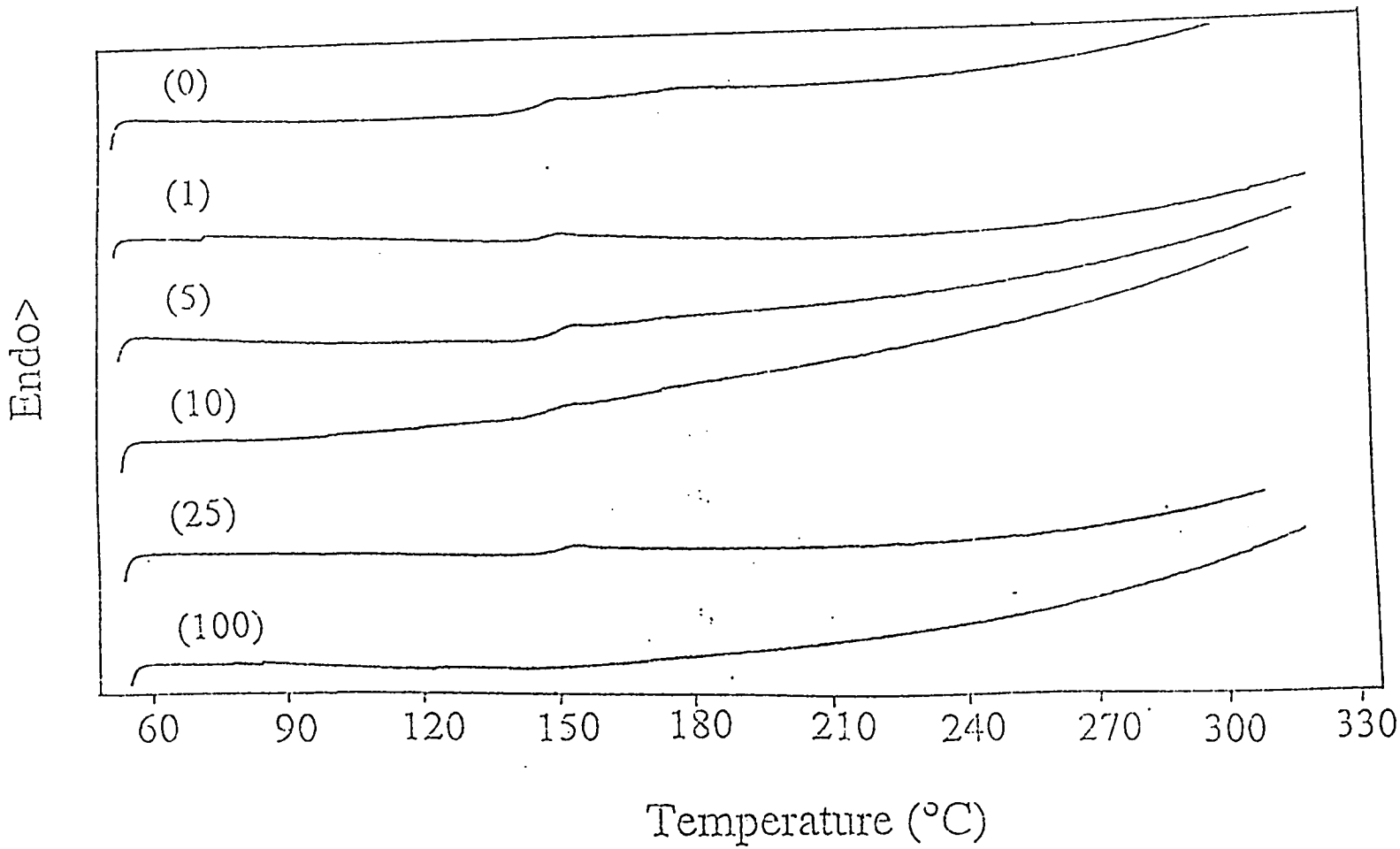


Fig. 12. DSC thermograms of LCP/PC composite at a heating rate of 20°C/min under argon atmosphere. The numbers in the brackets represents the weight percents of the LCP in the system.

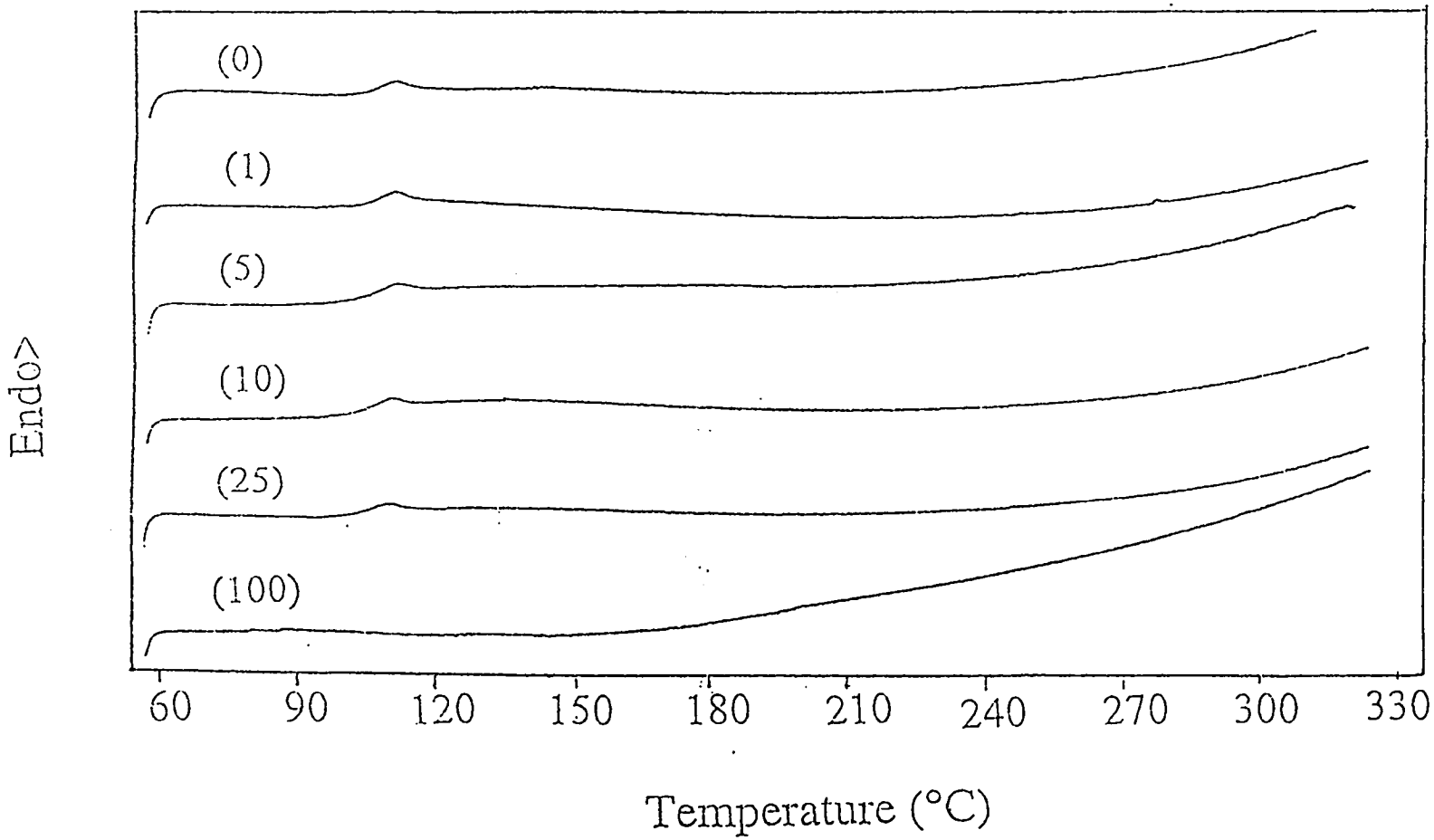


Fig. 13. DSC thermograms of LCP/PS composite at a heating rate of 20°C/min under argon atmosphere. The numbers in the brackets represents the weight percents of the LCP in the system.

Fig. 14 shows the thermograms of LCP/SPS system. T_g values of LCP/SPS composites were also around 100°C. Again, no prominent shift in T_g was observed.

4.4 MORPHOLOGICAL AND MECHANICAL CHARACTERIZATION

4.4.1 LCP/PS SYSTEM

LCP/PS system had two phase morphology with roundish LCP particles dispersed in the PS matrix as shown in Figs. 15 and 16. Size of the particles ranged from smaller than 1 μm to bigger than 5μm in diameter. The striking features are the sharp and distinct phase boundaries, the loose LCP material lying on the surface and the absence of polymer matrix on the LCP particles, all of which suggest poor interfacial adhesion. Processing at a higher temperature of about 270°C did not appear to make any difference in the morphology of the system.

The study on morphology was complemented by characterizing the associated tensile modulus and strength. Representative tensile stress-strain curves for LCP/polystyrene system at different compositions are given in Fig. 17. The experimental data are supplied in Appendix B. A composite with 25% LCP was also tried, but could not be molded. Poor interfacial adhesion between the LCP and polystyrene with wetting and mixing problems at high compositions is believed to be the reason for that. Composite modulus did not seem to change significantly with composition however tensile strength (and strain to

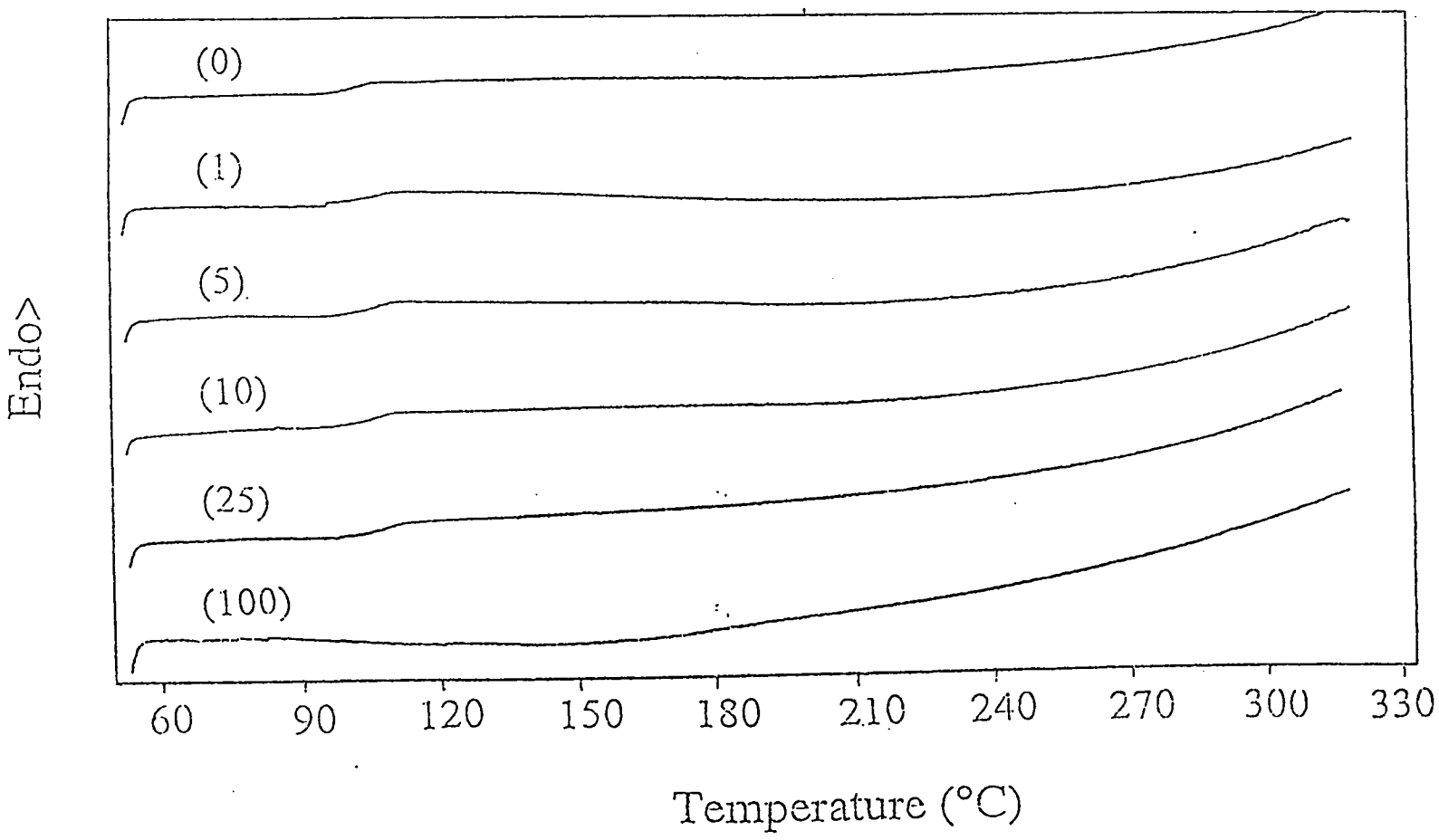


Fig. 14. DSC thermograms of LCP/SPS composite at a heating rate of 20°C/min under argon atmosphere. The numbers in the brackets represents the weight percents of the LCP in the system.

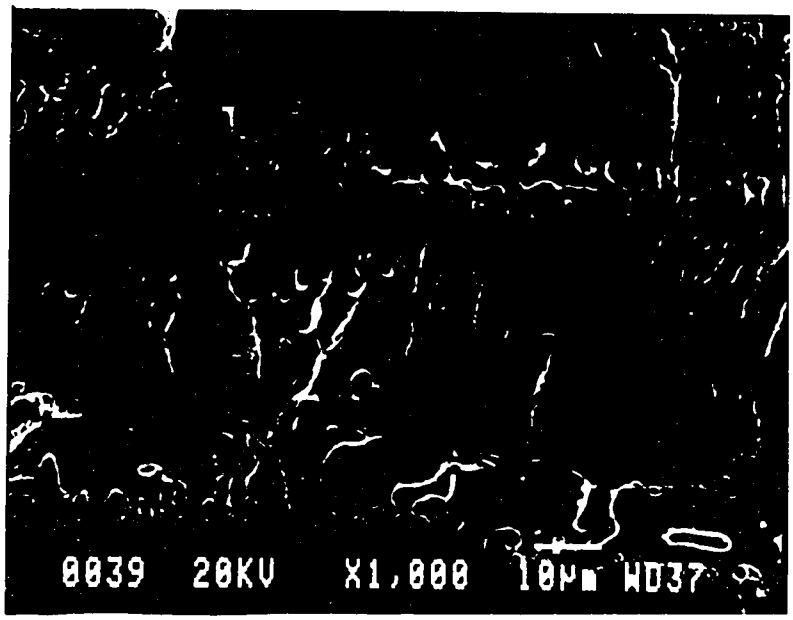


Fig. 15. Scanning electron microscopy of a fracture surface of LCP/PS system (with 10% LCP).

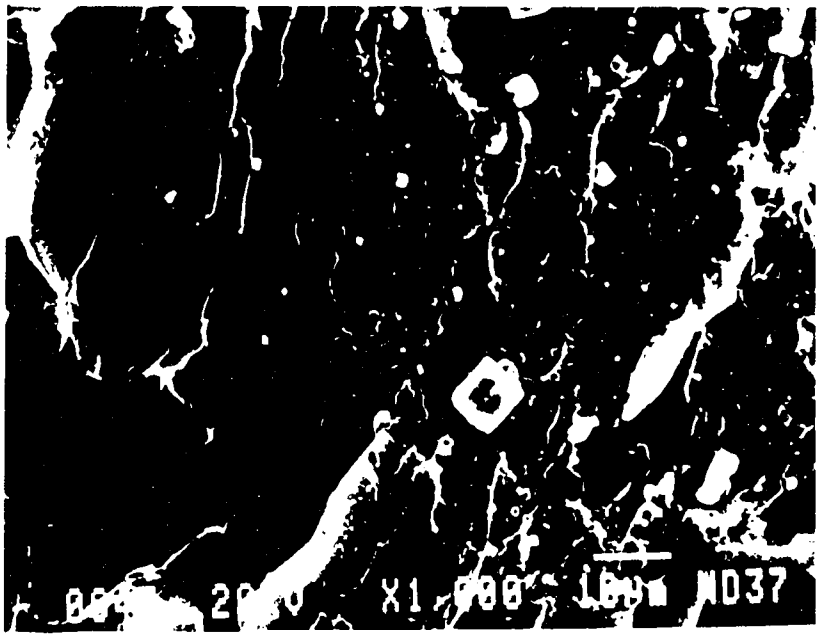


Fig. 16. Scanning electron micrograph of a fracture surface of LCP/PS system (with 10% LCP) showing the sharp interface boundary around an LCP particle.

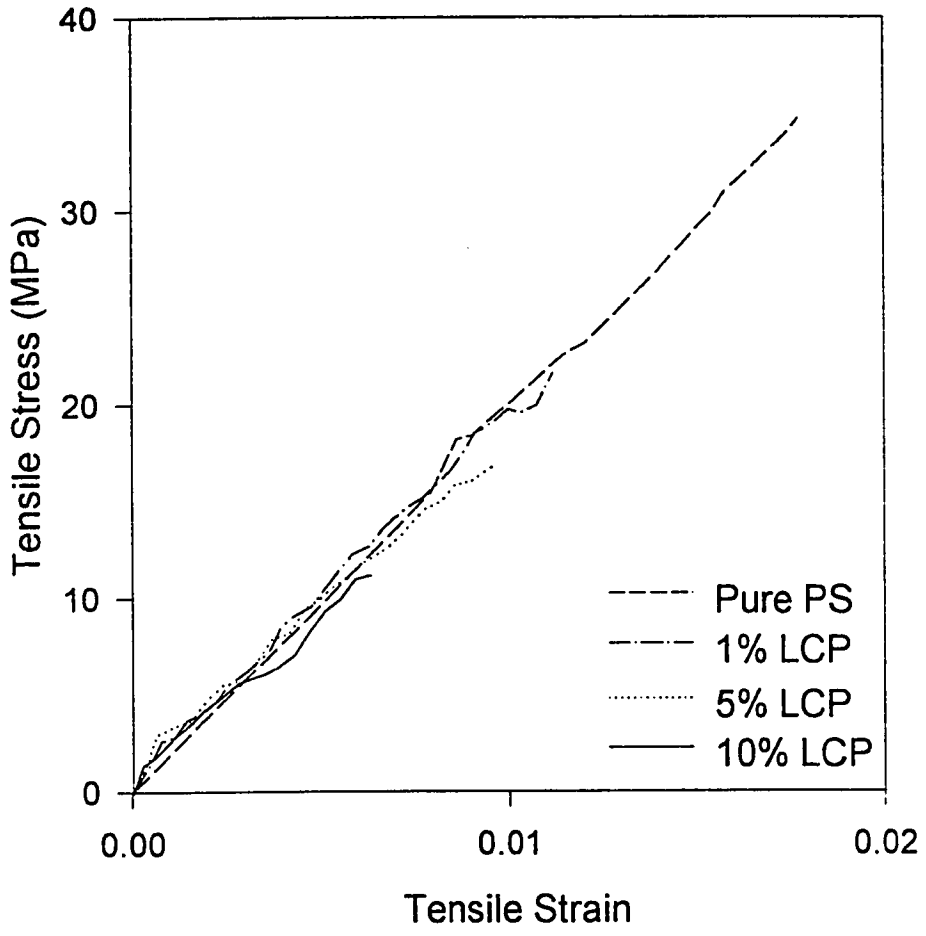


Fig. 17. Representative tensile stress-strain curves for LCP/PS system (compression molded at 225°C) at various compositions.

break) dropped dramatically with increase in LCP content. Plots of modulus and strength vs LCP content are given in Figs. 18 and 19, respectively. Also given in the plots is the prediction by the rule of mixtures for the case of no adhesion between the LCP and polystyrene. If the interfacial adhesion does not exist between the LCP and the thermoplastic, the volume occupied by the LCP can mechanically be regarded as voids and the simple rule of mixtures yields the following equations for the composite modulus (E_c) [Weidmann, 1990] and composite strength (σ_c) [Crevecoeur, 1990 and Crawford, 1987].

$$E_c=(1-V_f)E_m \qquad (1)$$

$$\sigma_c=(1-V_f)\sigma_m \qquad (2)$$

where V_f represents the volume fraction of the fiber (reinforcement), LCP, and σ_m and E_m are the tensile strength and modulus of the pure thermoplastic matrix, respectively.

Volume fractions were calculated from the weight fractions using specific gravities of the PS and LCP of approximately 1.05 and 1.5, respectively. Refer to Appendix C for calculation details.

Composite modulus values were close to the predicted values for the case of no interfacial adhesion between the LCP and the polystyrene. However the decrease in composite strength was much worse than the no bond prediction. This is understandable since the modulus is related to the stiffness of the material before fracture and it could be predicted reasonably well by the rule of mixtures for the case of no interfacial bonding. On the other hand composite tensile strength is a result of material fracture at the weakest point of the material and it could drop well beyond the prediction by the rule of mixtures

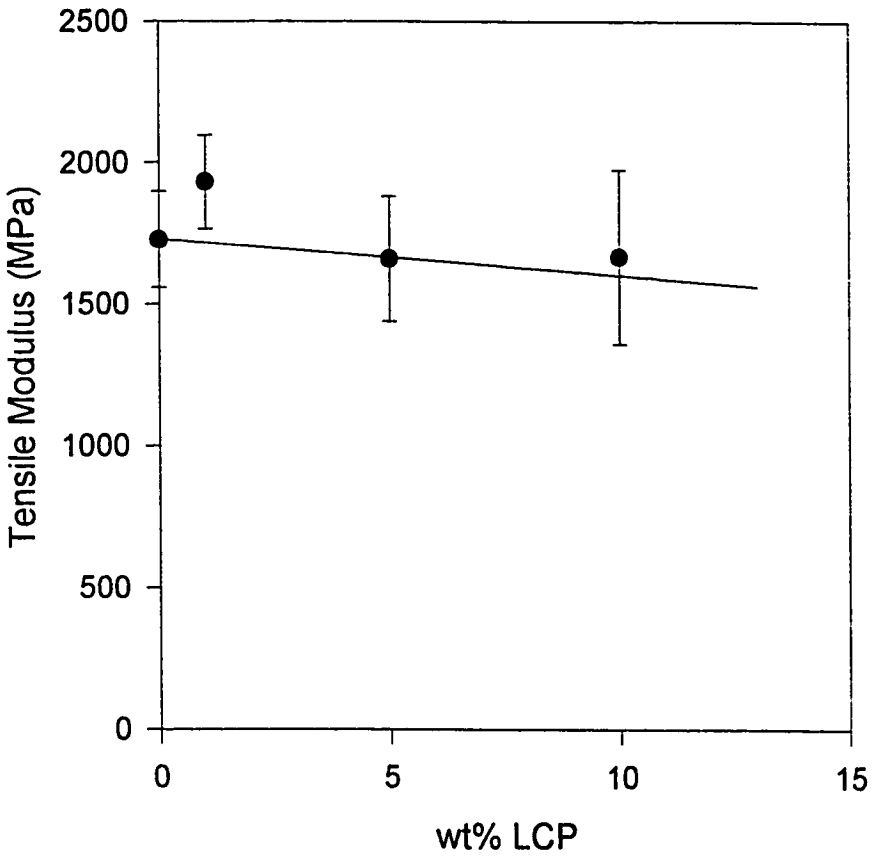


Fig. 18. Tensile modulus variation with LCP content for compression molded LCP/PS composite. The solid line corresponds to Eq. 1.

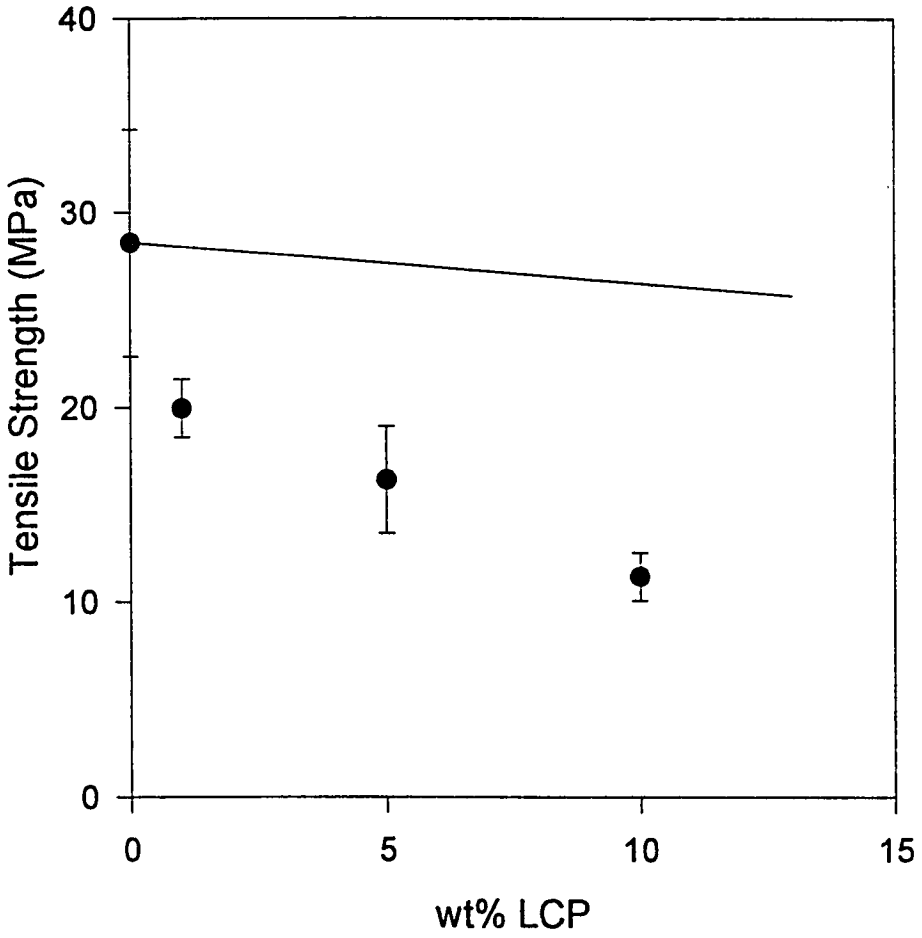


Fig. 19. Tensile strength variation with LCP content for compression molded LCP/PS composite. The solid line corresponds to Eq. 2.

for the case of lack of adhesion between the components of the composite. When there is no (or poor) adhesion between the LCP and the thermoplastic matrix, existence of the LCP particles will cause stress concentrations at the interfaces of the two components (this will happen after the bond fails at some stress level for the case of some interfacial bonding). This, especially around sharp edged LCP particles, could result in cracking and finally the failure of the material at a stress level quite below that predicted by utilizing the rule of mixtures in which the effect of discontinuities in the material is not taken into account.

Tensile tests were also performed on the LCP/PS system processed at 270°C (instead of 225°C), the results were not different (Fig. 20). Higher processing temperature did not appear to help interfacial bonding of LCP/PS composite. Composite modulus scattered about the prediction by the rule of mixtures for the no interfacial adhesion case (Fig. 21) and the composite tensile strength dropped again dramatically with increase in LCP content (Fig. 22).

4.4.2 LCP/SPS SYSTEM

Morphology of the LCP/SPS composite was not much different than the LCP/PS system. The interfaces between the LCP particles and the SPS matrix were also well defined (Figs. 23 and 24) indicating poor bonding between LCP and SPS. Sulfonation of PS which was determined to be only about 11% did not seem to improve the compatibility appreciably.

On the other hand being able to form a composite plate with 25% LCP while it was not possible (due to poor interfacial bonding) for the LCP/PS system suggests that there

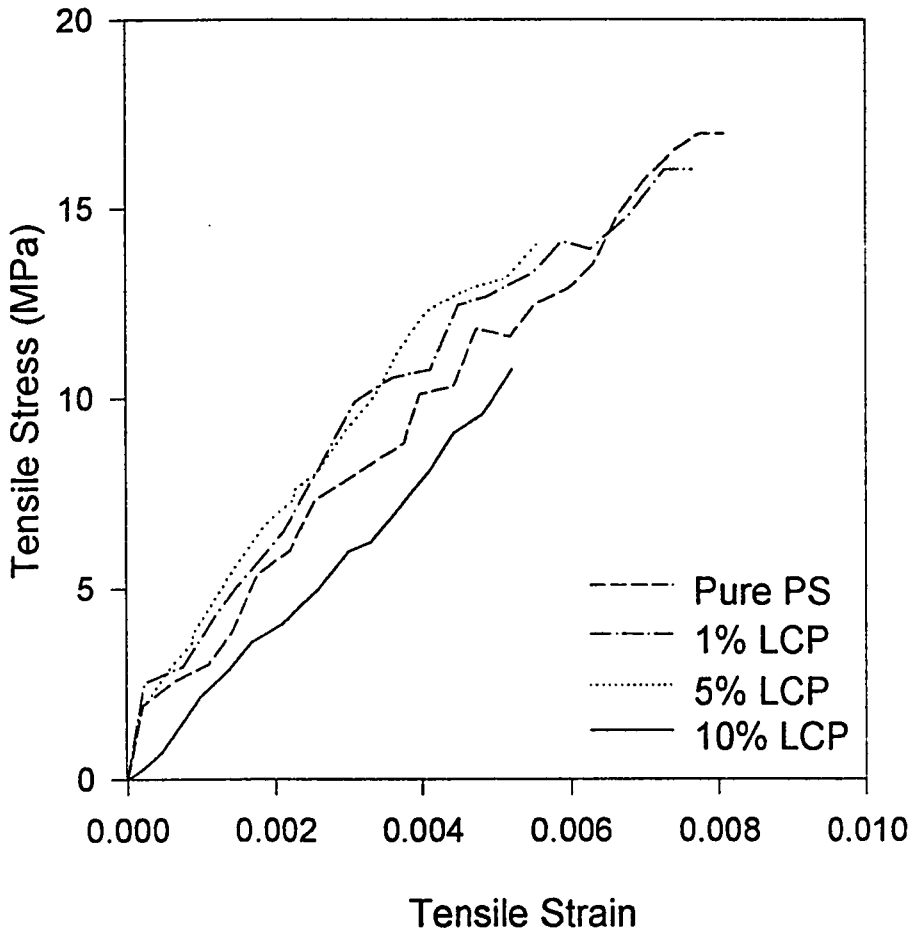


Fig. 20. Representative tensile stress-strain curves for the LCP/PS system (compression molded at 270°C) at various compositions.

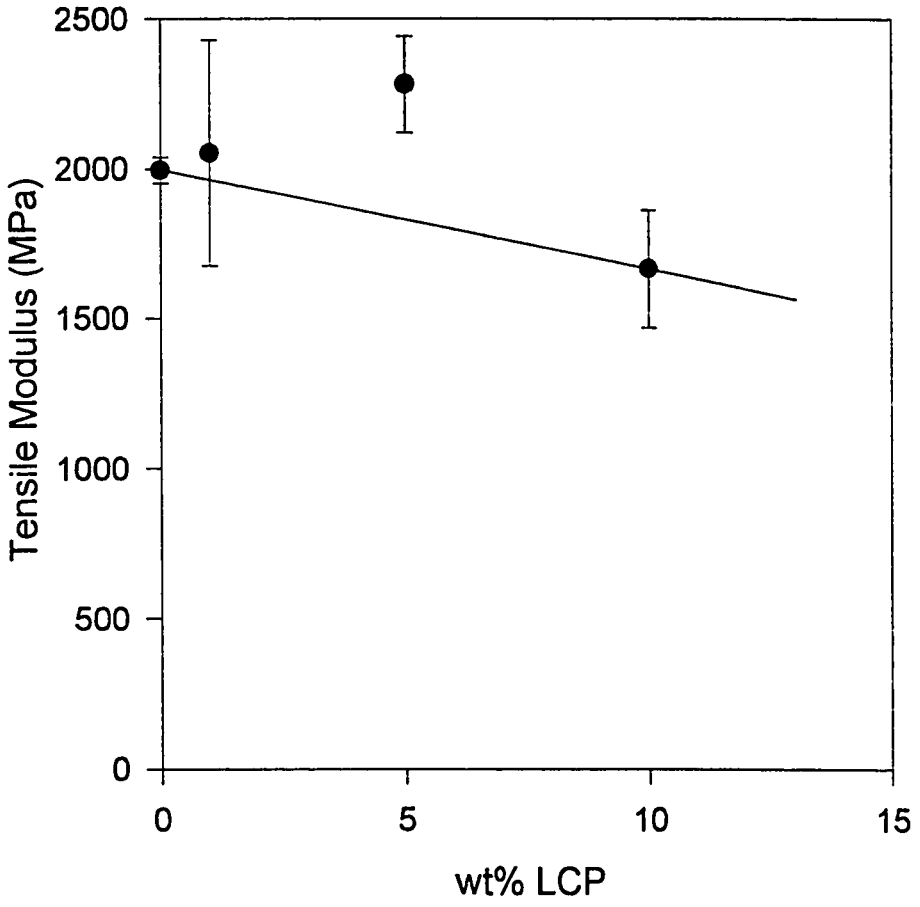


Fig. 21. Tensile modulus variation with LCP content for compression molded LCP/PS composite (processed at 270°C). The solid line corresponds to Eq. 1.

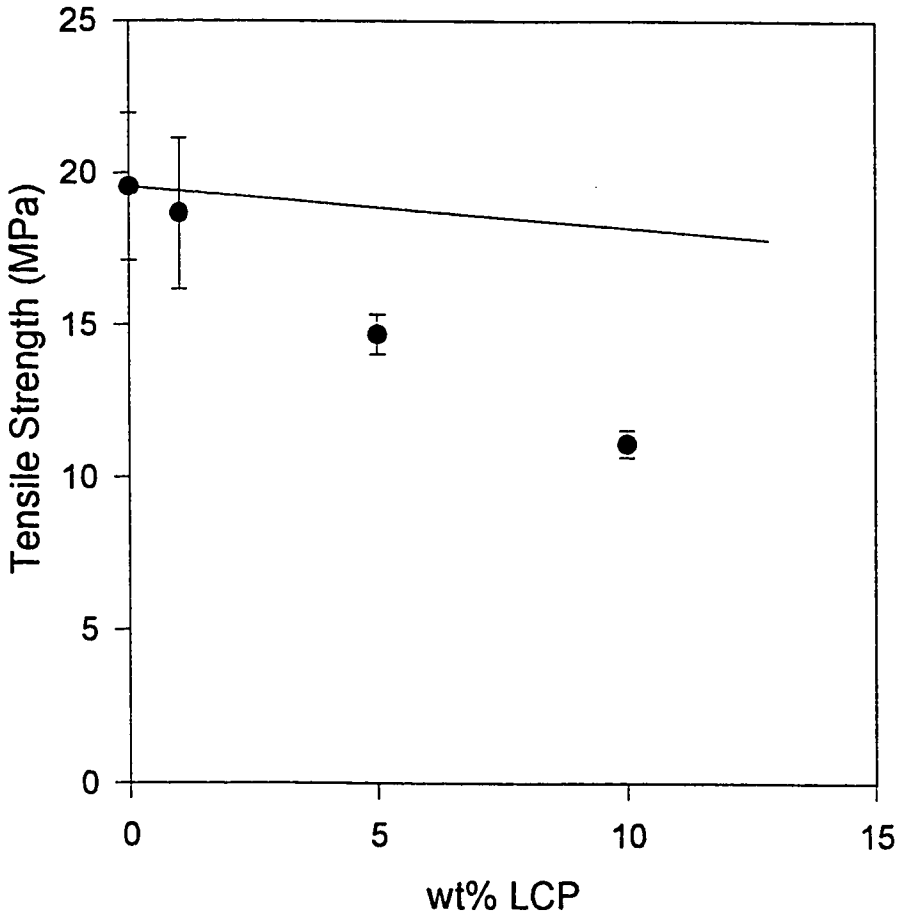


Fig. 22. Tensile strength variation with LCP content for compression molded LCP/PS composite (processed at 270°C). The solid line corresponds to Eq. 2.

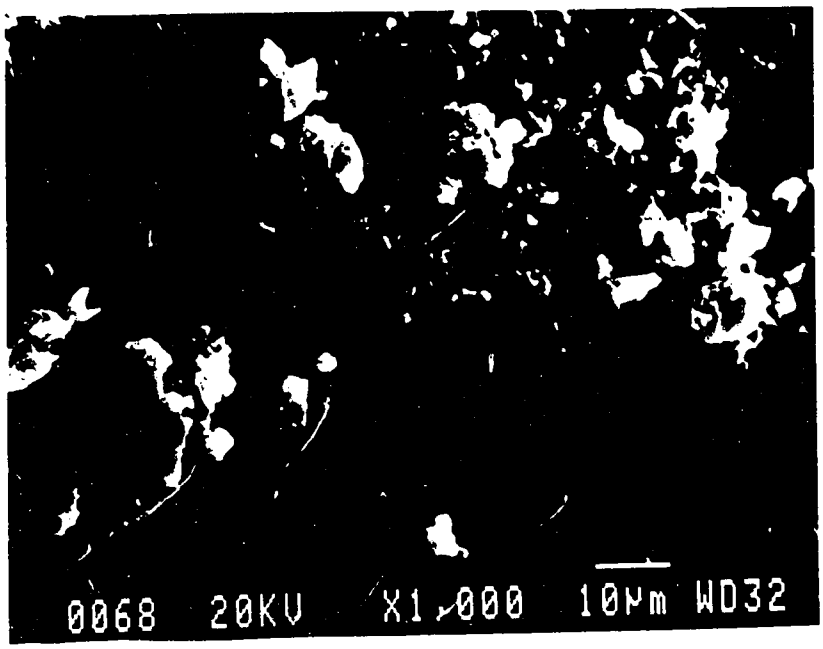


Fig. 23. Scanning electron micrograph of a fracture surface of LCP/SPS system (with 25% LCP).

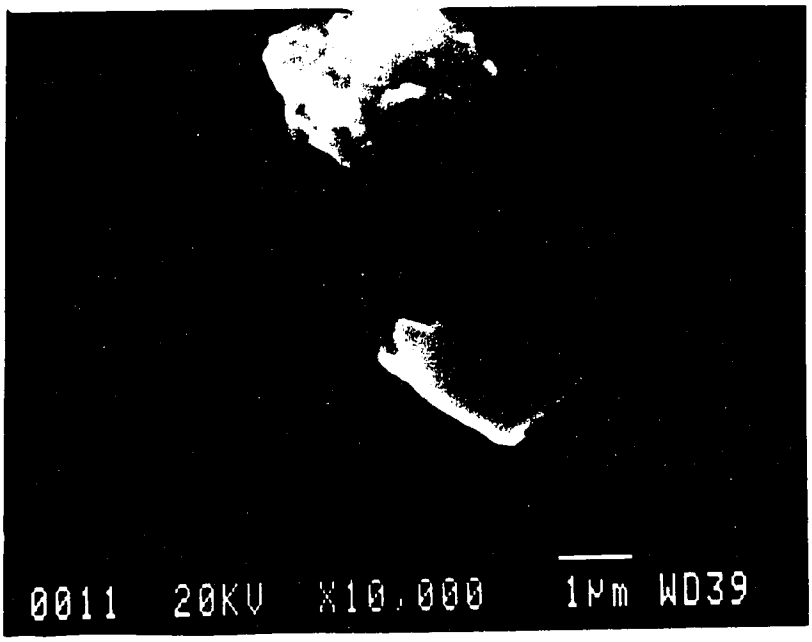


Fig. 24. Scanning electron micrograph of a fracture surface of LCP/SPS system (with 5% LCP) showing sharp interface boundaries around LCP particles.

should be some improvement in bonding between the LCP and SPS. However this claim is not supported by the SEM micrographs.

Compression molding by keeping the material system at the process temperature (215°C) for 1 h and 2 h did not appear to change the overall morphology of the system, however at least one LCP particle was found with not so well defined interface (Fig. 25) which might be an indication of some improvement in interfacial bonding.

Fig. 26 shows the effect of LCP addition on the mechanical behaviour of the LCP/SPS composite system. (Refer to Appendix B for the experimental data). Pure SPS matrix and also the LCP/SPS system with the lowest LCP content resulted in a rugged fracture surface with some degree of plastic deformation (Fig. 27), whereas plastic deformation was at an insignificant level for the PS used as received. Further LCP addition resulted in embrittlement of the LCP/SPS system decreasing the composite strength (Fig. 28) below that predicted by the rule of mixtures for the case of no interfacial adhesion due to the same possible reasons outlined above for the LCP/PS system. However composite strength for any composition was higher for the LCP/SPS system than the LCP/PS system (Fig. 29). Composite modulus on the other hand did not change significantly with LCP addition, even with the addition of 25% LCP (Fig. 30). Being able to form LCP/SPS composite with as much as 25% LCP without loosing the composite stiffness, whereas this was not possible for the LCP/PS system, indicates the existence of a better bonding between the LCP reinforcement and the SPS matrix than the LCP/PS system. However, the lowering of the composite strength with LCP addition suggests that the interfacial bond might have been improved over the LCP/PS composite but it is still weak.

Fig. 25. Scanning electron micrograph of a fracture surface of 5% LCP/SPS system (treated at the process temperature for 2 h) showing an LCP particle with not so sharp boundaries.

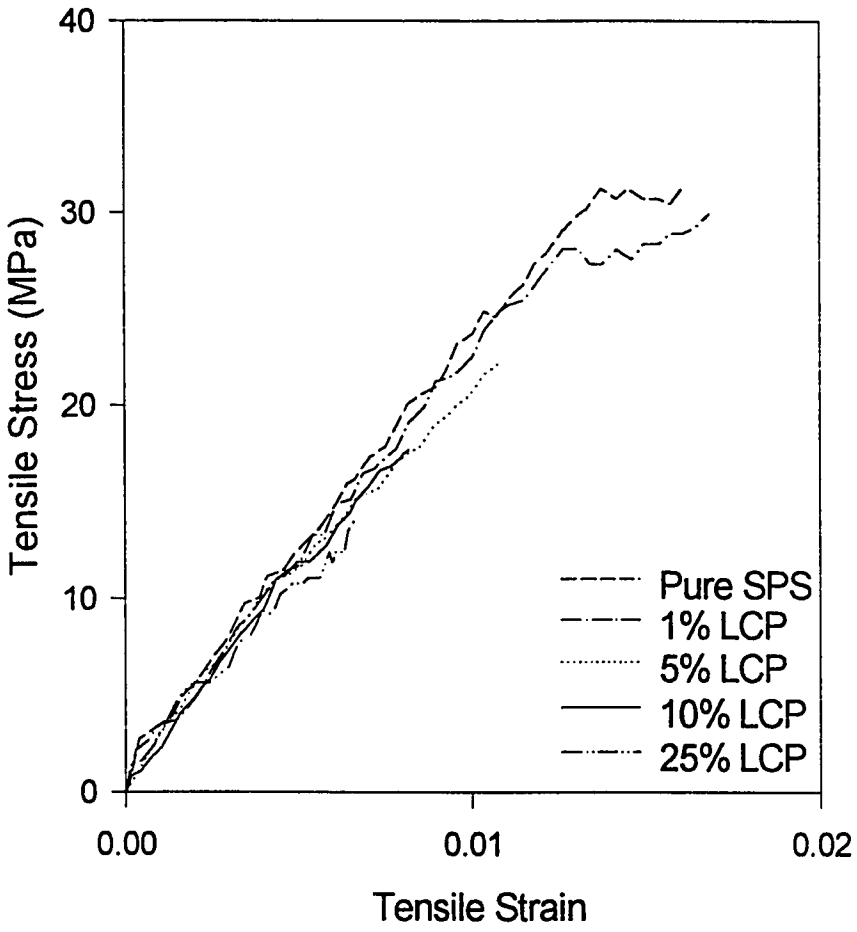


Fig. 26. Representative tensile stress-strain curves for LCP/SPS system (compression molded at 215°C) at various compositions.

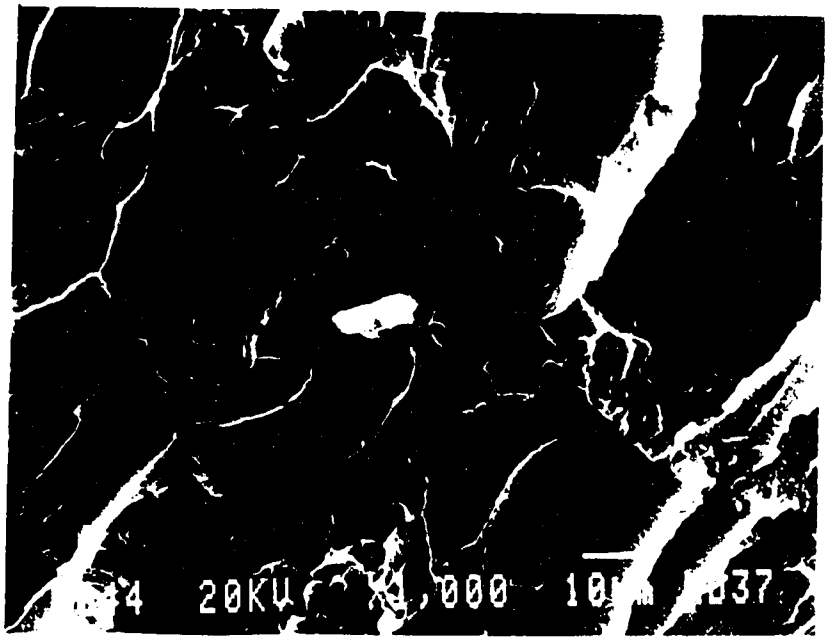


Fig. 27. Scanning electron micrograph of a LCP/SPS system (with 1% LCP) showing a rugged fractured surface with some degree of plastic deformation.

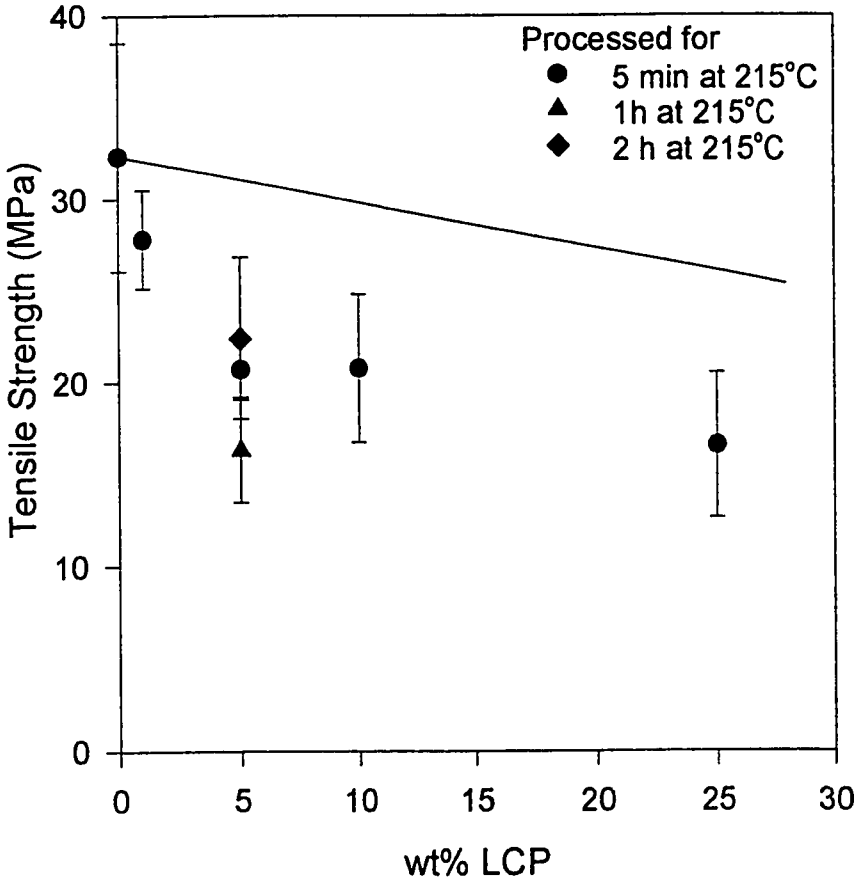


Fig. 28. Tensile strength variation with LCP content for compression molded LCP/SPS system. The solid line corresponds to Eq. 2.

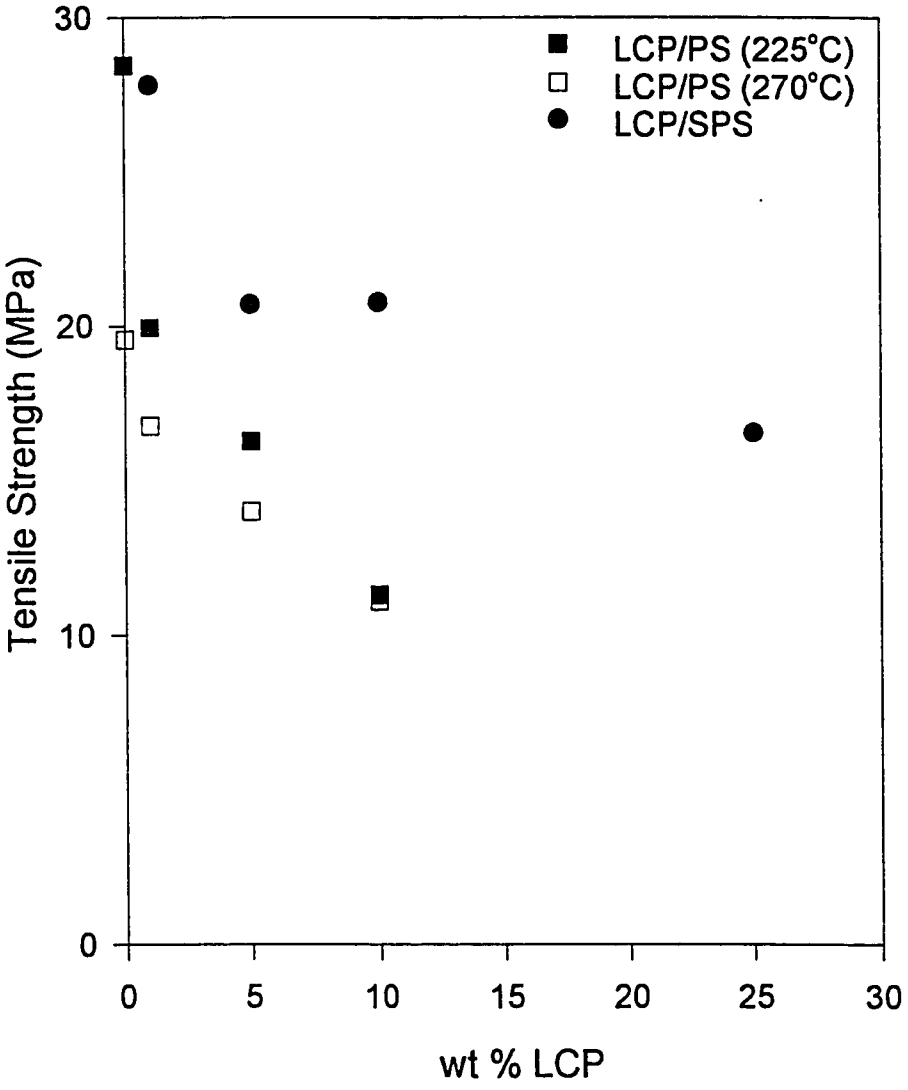


Fig. 29. Tensile strength variation with LCP content for compression molded LCP/PS and LCP/SPS systems. (The error bars were not included for clarity).

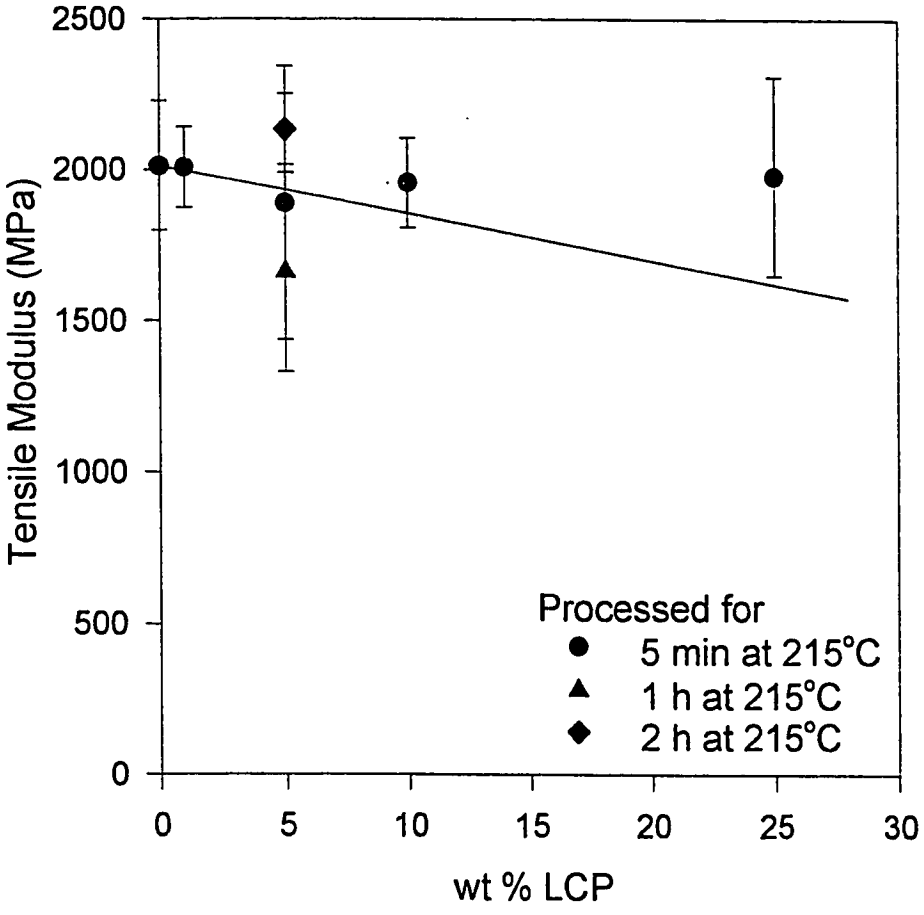


Fig. 30. Tensile modulus variation with LCP content for compression molded LCP/SPS system. The solid line corresponds to Eq. 1.

Heat treating the LCP/SPS composite (containing 5% LCP) at the compression molding process temperature for 1 h and 2 h did not seem to play an important role in the mechanical response of the material. As included in Figs. 28 and 30, composite modulus and strength were lowered by heat treatment of 1 h, but increased when heat treated for 2 h, over the system processed for about 5 min. The composite strengths for the two cases were still well below that predicted by the rule of mixtures for no interfacial adhesion case.

4.4.3 LCP/PC SYSTEM

LCP/PC system also had two phase morphology (Fig. 31). The interfaces between the LCP domains and PC matrix were not so well defined (Figs. 32 and 33) which has an indication of better interfacial adhesion than the LCP/PS and LCP/SPS systems. The LCP/PC system was compression molded also by keeping at the process temperature of 225°C for 1 h and 2 h (instead of 5 min) to see if a blend would form by dissolution of the LCP reinforcement in the PC matrix by heat treatment. But again a two phase morphology was formed similar to that of the composite system processed by holding at the process temperature for about 5 min (Fig. 31). Processing at a higher temperature of about 245°C also produced well bonded system (Fig. 34) however caused burning of the PC matrix at some parts of the mold as can be seen in Fig. 35, especially around LCP particles.

Compatibility of the LCP/PC system resulted in a significant improvement in the mechanical behaviour of PC by the addition of LCP (Fig. 36). (Experimental data are presented in Appendix B). Addition of LCP to PC generally increased the tensile modulus

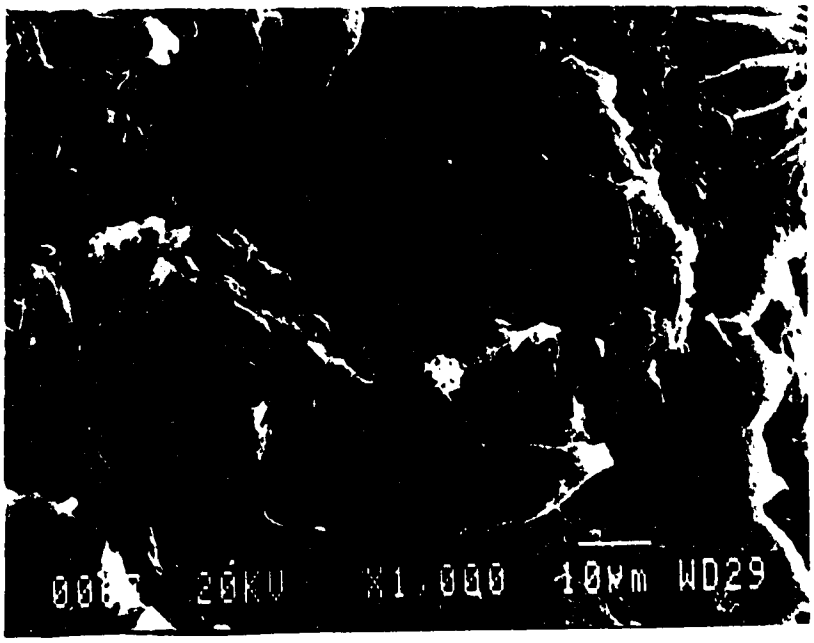


Fig. 31. Scanning electron micrograph of a fracture surface of LCP/PC system (with 25% LCP) showing a two phase morphology.

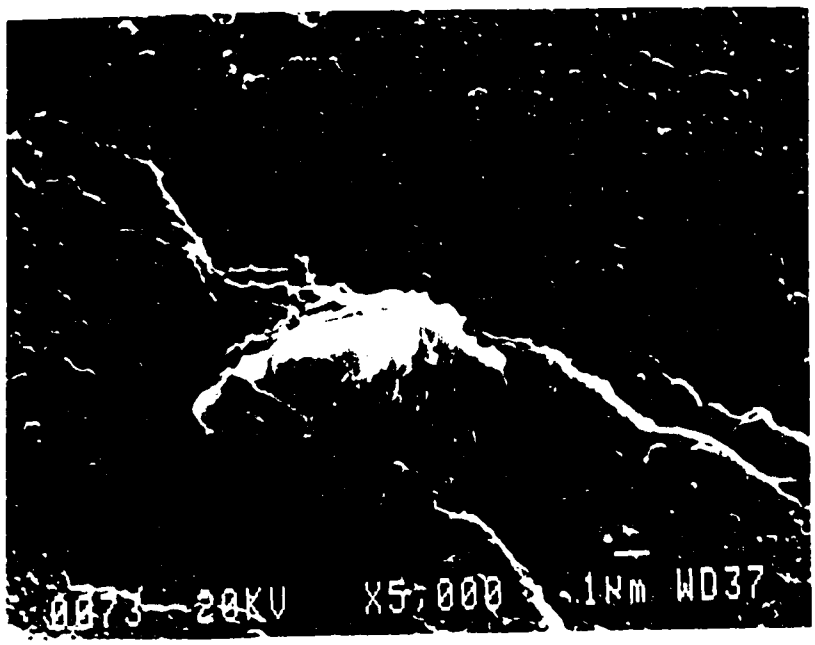


Fig. 32. Scanning electron micrograph of a fracture surface of LCP/PC system (with 1% LCP) showing not so well defined interfaces between an LCP particle and the PC matrix.

Fig. 33. Scanning electron micrograph of a fracture surface of LCP/PC system (with 25% LCP) showing not so distinct interfaces between the LCP domains and the PC matrix.

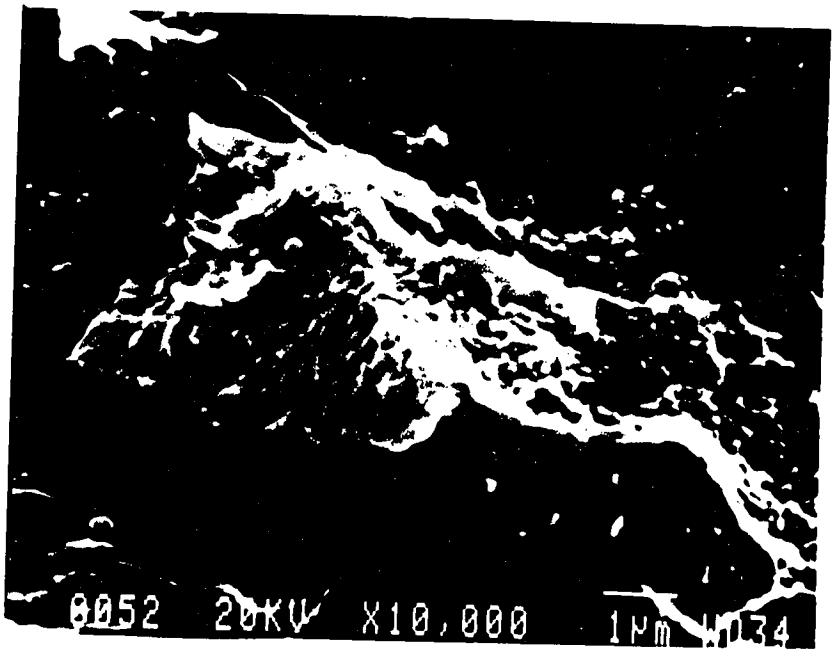


Fig. 34. Scanning electron micrograph of a fracture surface of LCP/PC system (with 5% LCP) showing a well bonded composite processed at 245°C)

Fig. 35. Scanning electron micrograph of a fracture surface of LCP/PC system (with 5% LCP) showing the burning of PC matrix especially around LCP particles.

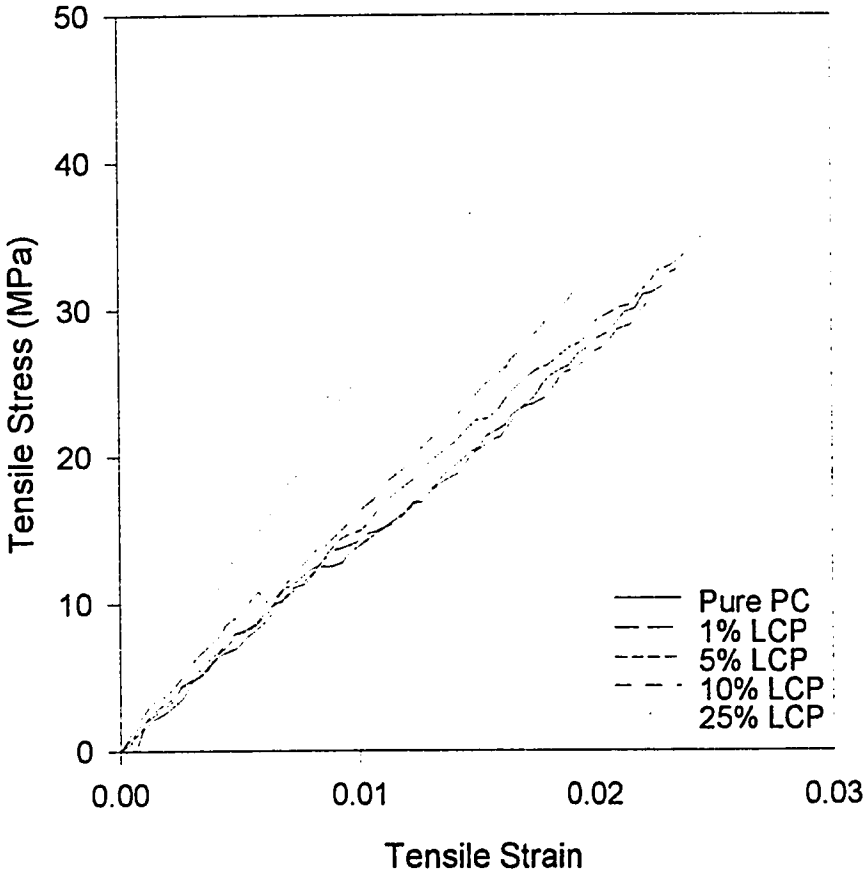


Fig. 36. Representative tensile stress-strain curves for the LCP/PC system (compression molded at various compositions).

(Fig. 37) and strength (Fig. 38) of compression molded plates. The improvement in composite strength was better for the LCP/PC system containing 5% LCP than the others. The reason for that might be the nonuniformities in mixing/dispersion causing wetting problems at high LCP concentrations. Accumulation of the LCP reinforcement at some parts of the composite due to nonuniform mixing/dispersion of LCP in PC can result in fracture at these weak points. An SEM micrograph from such a fracture surface is shown in Fig. 39. Non-uniformities in mixing-dispersion is also believed to be the reason of higher scatter for the composites with 5% or more LCP (Figs. 37 and 38).

Strength of the LCP/PC composite with 5% LCP was improved further when processed at a higher temperature of 245°C (Fig. 38). This could be an indication of an even stronger bonding between LCP and PC at this temperature. However similar improvement with temperature was not observed for the case of 25% LCP. Burning of the matrix especially around LCP particles, as mentioned above for the case of this higher processing temperature, would of course be more effective for composites with higher LCP concentrations. The composite strength however was still as good as that obtained when processed at the lower temperature of 225°C, which could also be an indication of further increase in the LCP/PC interfacial bonding with increase in process temperature.

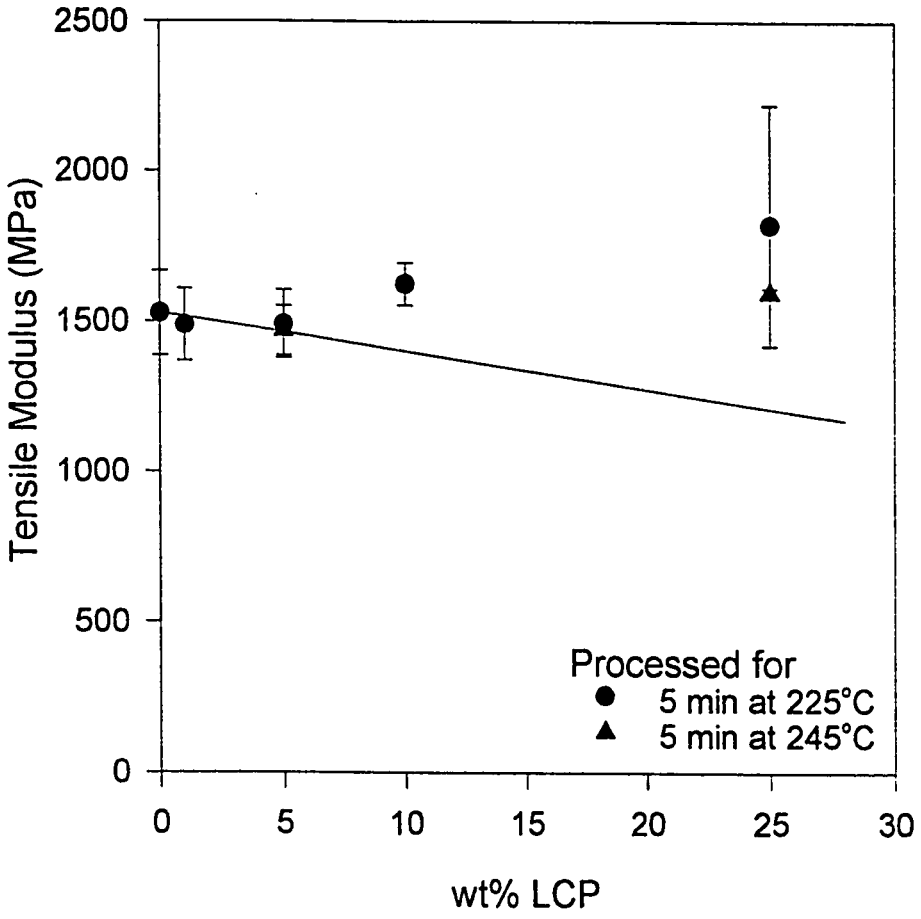


Fig. 37. Tensile modulus variation with LCP content for compression molded LCP/PC composite. The solid line corresponds to Eq. 1.

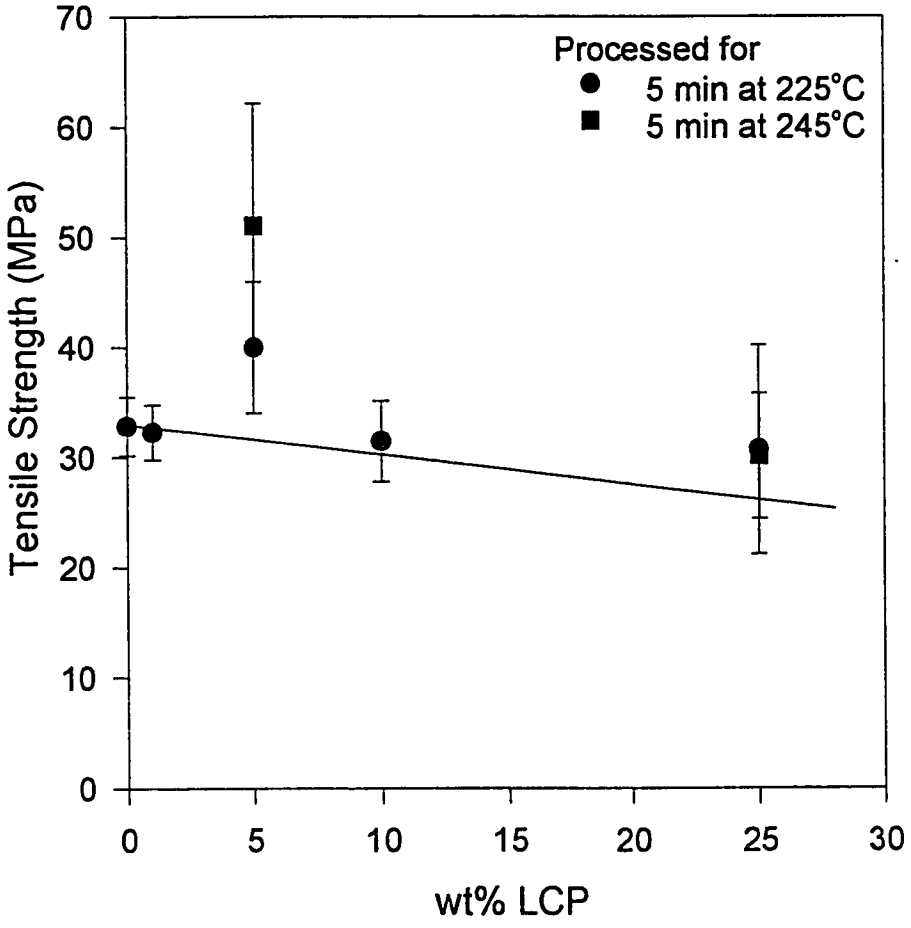


Fig. 38. Tensile strength variation with LCP content for compression molded LCP/PC composite. The solid line corresponds to Eq. 2.

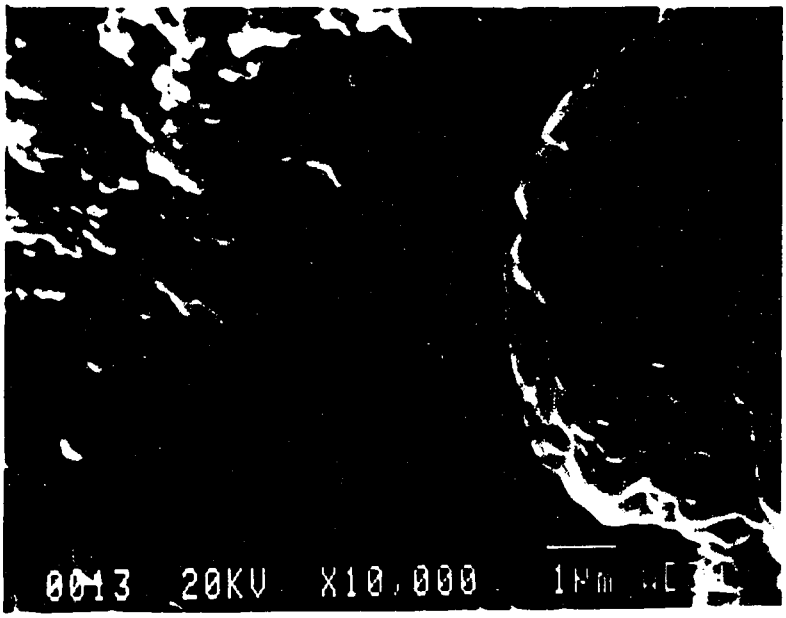


Fig. 39. Scanning electron micrograph of a fracture surface of LCP/PC system (with 25% LCP) showing non-uniform dispersion of LCP in PC matrix.

CHAPTER 5

CONCLUSIONS

The main aim of this research was to investigate the interfacial adhesion between a LCP and different thermoplastics. The LCP was synthesized at room temperature by interfacial polycondensation reaction between terephthaloyl chloride (TC) and dihydroxy diphenyl sulfone (DHDPS). The conversion of this reaction was more than 97%. The three thermoplastics used in this study were polycarbonate (PC), polystyrene (PS) and sulfonated polystyrene (SPS). SPS was formed to study the effect of the interacting group ($-SO_3H$) on the interfacial adhesion between LCP and SPS. Incorporation of $-SO_3H$ group to polystyrene was only about 5%. PS was also nitrated to form nitrated polystyrene (NPS). The nitration level of polystyrene went upto 97%. However LCP/NPS system could not be studied due to degradation of NPS during processing.

Compression molding technique was used to process the LCP/PC, LCP/PS and LCP/SPS at different weight fractions of LCP. Solution blending was also tried for each system, namely LCP/PC, LCP/PS and LCP/SPS. However, not a single common solvent was found so as to accommodate any of these systems.

The techniques used to study compatibility and interfacial adhesion in the LCP/PC, LCP/PS and LCP/SPS systems were differential scanning calorimetry (DSC), mechanical testing and scanning electron microscopy (SEM). The LCP was incorporated in the three

thermoplastics in weight percents of 1, 5, 10 and 25. However the 25% LCP/PS sheet could not be fabricated, possibly due to the lack of proper interfacial adhesion.

According to the DSC analysis, no glass transition temperature (T_g) was recorded for pure LCP in the operating temperature range of 50-320°C. From the thermograms obtained for LCP/PC, LCP/PS and LCP/SPS systems it was observed that the T_g values did not vary significantly within each system with the rise in LCP content.

SEM analysis of the LCP/PS composite formed at 225°C, showed a distinct two phase morphology. The interfaces between LCP particles and PS matrix were well defined. This suggested poor interfacial adhesion between LCP and PS matrix. The morphology of the system did not change when it was processed at a higher temperature of 270°C. The incompatibility of the LCP/PS system resulted in sharp decrease in the tensile strength of the LCP/PS composite with the increase in LCP content.

In the case of LCP/SPS the boundaries between LCP particles and SPS matrix were also sharp and well-defined indicating poor bonding between LCP and SPS. This indicated that 11% of sulfonation of polystyrene was not enough to improve the compatibility significantly. However a composite plate of 25% LCP/SPS was formed unlike in the case of 25% LCP/PS, which could be an indication of some improvement in bonding between LCP and SPS.

5% LCP/SPS system was also processed for 1 h and 2 h. However overall morphology of the system did not seem to change much except in one SEM micrograph the boundaries of LCP particle were not well defined indicating a chance of some improvement in interfacial bonding.

The strength of LCP/SPS system also decreased with increase in LCP content. However composite strength for any composition was higher for the LCP/SPS system than the LCP/PS system.

For the case of LCP/PC system processed at 225°C, again a two phase morphology was observed, but the interfaces between LCP domains and the PC matrix were not so sharp indicating better interfacial adhesion than the previous two systems studied. Processing the LCP/PC system at 245°C also revealed a well-bonded system, but also resulted in burning of the PC matrix, especially around the LCP particles.

There was a prominent increase in the tensile modulus and strength of the LCP/PC system with addition of LCP, as compared to LCP/PS and LCP/SPS systems.

CHAPTER 6

RECOMMENDATIONS

- The possibility of synthesizing the LCP as meltable (i.e processable in the melt state) should be studied by introducing flexible spacers, side chains or kinks in the main chain of the LCP molecule.
- The possibility of solution blending of the LCP with thermoplastics should be checked further by trying mixture of solvents.
- Further work can be done by utilizing extrusion or injection molding processing techniques. For these methods, a meltable LCP is essential and both the LCP and the thermoplastic should be in larger quantities. Due to high shear rates used in these techniques, the meltable LCP can be orientated in fibril form thus imparting high modulus and strength to the LCP/thermoplastic system in the direction of orientation.
- Interfacial adhesion between LCP and the thermoplastic might be improved further by

  (a) increasing the density of the functional groups in the LCP molecule.

  (b) incorporating strong interaction groups such as OH in the thermoplastic.

  (c) incorporating strong ionic groups such as $SO_3^- Na^+$ in the thermoplastic.

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Appendix A

Density estimation for pure PS

Density for pure PS was estimated by weighing a rectangular piece of PS sheet and measuring its volume (i.e., its length, width and height).

$$Mass = 0.2807\ g$$

$$Volume = 0.07 \times 2.542 \times 1.518 = 0.270\ cm^3$$

$$Density = \frac{Mass}{Volume} = \frac{0.2807}{0.270} = 1.04 g / cm^3$$

Density estimation for pure SPS

Density for pure SPS was also estimated by the same procedure outlined above.

$$Mass = 0.1508 g$$

$$Volume = 0.075 \times 1.084 \times 1.767 = 0.1436\ cm^3$$

$$Density = \frac{Mass}{Volume} = \frac{0.1508}{0.1436} = 1.05 g / cm^3$$

Density estimation for pure PC

Likewise the density for pure PC was determined by following the same procedure.

$$Mass = 0.4218\,g$$

$$Volume = 0.125 \times 1.760 \times 1.734 = 0.3815\,cm^3$$

$$Density = \frac{Mass}{Volume} = \frac{0.4218}{0.3815} = 1.105\,g/cm^3$$

Density estimation for pure LCP

Since pure LCP plate could not be fabricated, its density was estimated from the difference between the densities of 25% LCP/PC and 25% LCP/SPS sheets and the densities of pure thermoplastics determined earlier. An arithmetic average of the two values was taken as the LCP density.

25% LCP/PC

$$M = 0.3910\,g$$

$$V_{25\%LCP/PC} = 0.32cm^3$$

$$V_{25\%LCP/PC} = V_{PC} + V_{LCP} = \frac{M_{PC}}{\rho_{PC}} + \frac{M_{LCP}}{\rho_{LCP}} = \frac{(0.75)M}{\rho_{PC}} + \frac{(0.25)M}{\rho_{LCP}}$$

$$0.32 = \frac{(0.75)(0.3910)}{1.15} + \frac{(0.25)(0.3910)}{\rho_{LCP}}$$

$$\therefore\ \rho_{LCP} = 1.50\,g/cm^3$$

25% LCP/SPS

$$M = 0.2103\,g$$

$$V_{25\%\,LCP/SPS} = 0.186 cm^3$$

$$V_{25\%\,LCP/SPS} = V_{SPS} + V_{LCP} = \frac{M_{SPS}}{\rho_{SPS}} + \frac{M_{LCP}}{\rho_{LCP}} = \frac{(0.75)M}{\rho_{SPS}} + \frac{(0.25)M}{\rho_{LCP}}$$

$$0.186 = \frac{(0.75)(0.2103)}{1.05} + \frac{(0.25)(0.2103)}{\rho_{LCP}}$$

$$\therefore\ \rho_{LCP} = 1.46\,g/cm^3$$

Then the average value for ρ_{LCP} is

$$\rho_{LCP} = \frac{1.50 + 1.46}{2} = 1.48 g/cm^3$$

Appendix B

LCP/SPS	Tensile Modulus (MPa)	Tensile Strength (MPa)	Tensile Strain (-)
0/100			
A	2071.0000	34.5460	0.0208
B	1775.6340	39.0476	0.0265
C	2192.3600	31.3280	0.0161
D	2012.66	24.2200	0.0238
1/99			
A	2110.5500	25.5130	0.0117
B	1892.8100	25.4500	0.0173
C	2137.6500	29.9496	0.0168
D	1892.9000	30.2897	0.0206
5/95			
A	2236.2780	21.7600	9.3778e-3
B	1454.3000	20.0774	0.0133
C	2322.2200	22.1298	9.1778e-3
D	1548.8100	18.8800	0.0118
10/90			
A	1925.7900	17.7180	0.0110
B	1758.4500	16.9800	9.1778e-3
C	2071.8000	25.1330	0.0147
D	2071.2700	23.2134	0.0220
25/75			
A	1696.6310	15.8470	9.2889e-3
B	2323.5900	22.3200	9.1778e-3
C	2197.4800	13.9089	6.1778e-3
D	1700.0000	14.0670	8.2000e-3

LCP/PS	Tensile Modulus (MPa)	Tensile Strength (MPa)	Tensile Strain (-)
0/100			
A	1554.0620	27.9980	0.0161
B	1645.0450	30.2707	0.0220
C	1767.0000	34.7652	0.0262
D	1947.7060	20.7417	0.0122
1/99			
A	2005.3470	20.2217	0.0110
B	1705.4230	19.7602	0.0121
C	1931.8600	21.6870	0.0112
D	2088.8200	18.0778	8.4000e-3
5/95			
A	1517.4200	18.8850	0.0126
B	1718.0000	16.8000	0.0102
C	1458.6000	17.0237	0.0115
D	1949.8000	12.4028	6.2889e-3
10/90			
A	1517.4200	10.0500	6.8660e-3
B	1718.0000	11.2100	6.8440e-3
C	1458.6000	12.9828	7.1778e-3
D	1949.8000	10.9350	5.6220e-3

LCP/PC	Tensile Modulus (MPa)	Tensile Strength (MPa)	Tensile Strain (-)
0/100			
A	1665.6250	29.3487	0.0208
B	1617.1340	33.5741	0.0205
C	1363.4250	32.6680	0.0236
D	1461.9900	35.7327	0.0240
1/99			
A	1488.0000	32.0000	0.0116
B	1608.0000	35.0000	0.0107
C	1368.0000	29.0000	0.0129
D		33.0000	0.0195
5/95			
A	1544.5200	33.4400	0.0218
B	1604.0600	43.3300	0.0286
C	1344.1230	36.7216	0.0262
D	1469.6400	46.5295	0.0306
10/90			
A	1560.5000	31.8264	0.0197
B	1578.4600	36.0181	0.0226
C	1639.1100	30.8000	0.0218
D	1716.5270	27.1080	0.0171
25/75			
A	2421.7900	44.9153	0.0183
B	1612.5000	27.1591	0.0161
C	1654.0800	25.3900	0.0203
D	1600.0000	25.3116	0.0151

Appendix C

Conversion of Weight Fraction to Volume Fraction

To use the rule of mixtures equation (for the case of no interfacial adhesion) it was necessary to convert the known LCP weight fraction values (W_f) to LCP volume fraction values (V_f), as follows:

$$V_f = \frac{V_{LCP}}{V_{total}} = \frac{W_f / \rho_f}{\frac{W_f}{\rho_f} + \frac{W_m}{\rho_m}}$$

But

$$W_f = w_f W_{total}$$

Therefore

$$V_f = \frac{w_f W_{total}}{\rho_f \left(\frac{w_f W_{total}}{\rho_f} + \frac{w_m W_{total}}{\rho_m} \right)}$$

or

$$V_f = \frac{w_f}{\rho_f \left(\frac{\rho_m w_f + \rho_f w_m}{\rho_f \rho_m} \right)}$$

Simplifying it further

$$V_f = \frac{\rho_m w_f}{\rho_m w_f + \rho_f w_m}$$

or since $w_m = \left(1 - w_f\right)$

$$V_f = \frac{\rho_m w_f}{\rho_m w_f + \rho_f \left(1 - w_f\right)}$$